CHEMICAL ABSTRACTS

Vol. 15. SEPTEMBER 20, 1921 No. 18

1—APPARATUS

C. G. DERICK

A comparative study of fractionating still-heads. NEIL P. MOORE. *J. Phys. Chem.* **25**, 273–303(1921).—The object was to det. the factors which must be controlled in order to effect a better sepn. of the components of a mixt. by a single distn. A brief outline of the literature is given, after which a procedure for the sufficiently accurate analysis of binary liquid mixts. by the refractometric method, without the necessity for temp. control, is explained. An app. is described in which it was found possible to study the relative efficiencies of fractionation in a cylindrical still-head under a variety of conditions. Data are given on these efficiencies when a mixt. of 75% $CHCl_3$ and 25% CCl_4 was fractionated. A practical analysis of the process of fractional distn. into certain factors which seem to be of primary importance was made from these results and those of other investigators. A *new type of still-head*, which was flat with numerous slotted angle-strips on the bottom, was designed for the purpose of studying the influence of these factors, and is described in detail. Working with this app. under easily obtainable conditions, it was found possible to increase the efficiency from the best obtainable with any type of cylindrical head studied (47.8%) to 82.7%.

C. C. VAN VOORHIS

Mill for colloidal comminutioo in industrial chemical work. C. NASKE. *Z. Ver. deut. Ing.* **65**, 495–6(1921); cf. *C. A.* **15**, 1584.—The characteristics and importance of org. colloids as regards plant nutrition, and of inorg. colloids as regards ceramics, colors, photography, etc., are discussed. Methods of prepg. dispersions may be either by elec. or mechanical means. A hammer mill has the disadvantages that an increase in speed increases the air resistance; much heat is evolved to no purpose; and the finest particles, which should be further subdivided, escape the beaters and are carried through the gratings with the air stream. A ball mill has the disadvantages that the velocity of fall of the balls is small, the work done per blow small and the number of blows, few. Hence, an impractical length of time is required for colloidal comminution. Plauson's "Colloidmill" first made possible the mechanical prepn. of dispersoids on a large scale by modifying a hammer mill so that the beater arms impinged on a liquid surface. P. further operated the rotor at very high peripheral speed to increase the number of blows per unit of time. Two cross sections of the mill are shown. It consists of a water-cooled cylindrical casing with axis horizontal, and an eccentrically mounted rotor whose projections work past similar projections fixed on the casing and on an adjustable bottom bed plate. When the rotor is operated at a high speed the liquid is flung off the rotor and again sucked in bringing fresh particles into contact. The centrifugal force also sets up a rotation of the liquid in the casing. The suspension to be ground enters at the top and is discharged at the bottom of one side. A very powerful hammering action is obtained. Heat and elec. effects assist in the comminution, the latter tending to keep the fine particles sepd. Difficulties as regards shaft packing and strength of parts have been partially overcome, the latter by using "spring steel plate." A fineness of 0.3 μ is obtained at 20, of 0.1 μ at 30 and colloidal

size at 40 m. per sec. Two plant layouts are shown in one of which *cellulose sheets* were prepared of 3.5 mm. thickness, capable of withstanding 55000 v., of 300–500 kg. per sq. cm. breaking strength. In the other the yield of *oil from oil shale* was increased from 8% by distn. to 12–14% by colloidal comminution and decantation. Further possibilities are discussed as regards treating *oil cake, manuf. of colloidal fuel, pigments, lakes, and phosphates.* C. C. HERITAGE

Air pump capacity and design. GAVIN A. RENTON. *Chem. Trade J.* **69**, 61-62 (1921); 4 fig.—R. describes how to calc. the volumetric capacity of a vacuum pump. H. BUTTLER

Exeter rotary pump suitable for high heads. S. H. FARKAS. *Elec. Rev.* (Chicago) **79**, 217–8(1921).—A detailed illus. account of an improved pump especially suitable for handling oil, molasses, mine water, tar, chemicals, paints, turpentine, gasoline, soaps, etc. The pump is self-priming. C. G. F.

Viscosimeter calibration and conversion chart. ANON. *Lubrication* **7**, No. 5, 5–8 (1921).—Calibration of the Saybolt Universal No. 20, Saybolt Furol No. 32, Redwood Standard No. 1326, Redwood Admiralty No. 737, Engler No. SR–2607, and Barbey instruments makes it possible to convert from one to the other and to absolute kinematic viscosities. The instruments were calibrated by the use of alcohol-water mixts., castor oil, glycerol-water mixts., and mineral oils, the last having been measured on the Barbey viscosimeter. The Barbey instrument is the only one which gives a linear relation between its readings and the kinematic viscosity. However, different Barbey instruments do not have the same instrument constant; this may be due to its being standardized with raw rapeseed oil at 35° to give a reading of 100, which is hardly a fixed standard. EUGENE C. BINGHAM

Recent modifications in the construction of platinum resistance thermometers. T. S. SLIGH, JR. Bur. Standards, *Sci. Papers* No. **407**, 63pp.(1921).—See *C. A.* **15**, 1423. W. P. WHITE

Constant-temperature baths. "OMEGA." *Chem. Trade J.* **69**, 30(1921).—A list is given of 15 mixts. for const.-temp. baths and requiring little attention for boiling temps. from 40° to 300°. For the lowest temp. a mixt. of 98% EtBr and 2% EtOH is used and for the highest temp. 90% cottonseed oil and 10% beeswax. W. H. BOYNTON

Application and use of immersion electric heaters. JOHN M. STRAIT. *Elec. Rev.* (Chicago) **79**, 161–3(1921); 4 illus.—A detailed account, including instructions for properly installing, selection of correct size of unit, tabulation of losses by radiation from hotwater tanks, watts capacity required for tanks of various sizes, etc. C. G. F.

New sugar refractometer (SCHULZ) **28.** Simmance recording calorimeter (WOOD) **21.**

HAUSBRAND, E.: **Die Wirkungsweise der Rektifizer- und Destillierapparate.** Berlin: Jul. Springer. M 64. For review see *Chem. App.* **8**, 116(1921).

PARNICKE, A. AND CAMPAGNE, EM.: **L'appareillage mecanique des industries chimiques.** Paris: Dunod 47 quai des Grands-Augustins. 356 pp. 34 f. For review see *Rev. sci.* 59, 288(1921).

Gas-washing apparatus. H. NIELSEN and F. D. MARSHALL. U. S. 1,378,716, May 17.

Acetylene generator. E. LUDER. U. S. 1,377,595, May 10.

Apparatus for generating hydrogen sulfide or other gases and for treating solutions with the gas. H. R. HANLEY. U. S. 1,377,478, May 10. A tank adapted for the

treatment of metal salt solns. (*e. g.*, $ZnSO_4$) with a gas such as H_2S is connected in closed circuit with the gas generator and means are provided for maintaining a reduced pressure in the generator. Cf. *C. A.* **15**, 563.

Apparatus for treating gases with finely divided solids. P. POORE. Brit. 162,769, Feb. 2, 1920. App. is specified for carrying out processes in which material in a finely divided state is used and which may be applied to the carbonization of sawdust or other finely divided carbonaceous material or to a lime purifier or to any process in which contact is required between fluids and solids in a finely divided state. Cf. *C. A.* **14**, 1912.

Heating gases and liquids. AKTIEBOLAGET LJUNGSTRÖMS ANGTURBIN. Brit. 162,250, Apr. 21, 1921. Relates to app. for transferring heat from one gas or liquid to another as from furnace gases to air for combustion, from the foul air of a room to fresh air for ventilation, or from warm to cold H_2O when changing the H_2O in swimming-baths. A suitable construction is specified.

Respirators; testing gases. L. A. LÉVY and R. H. DAVIS. Brit. 163,102, Feb. 9, 1920. Combined with a respirator is an app. for the detection of small quantities of CO, comprizing a chamber inclosing a reagent such as iodine pentoxide, capable of generating in the presence of CO an irritant or lachrymatory vapor such as iodine, which travels with the inspired gases and warns the wearer of the approaching exhaustion of the respirator. The respirator and detector app. are contained in a single casing but they may be sepd. and joined by a tubular connection; the respirator proper comprizes a drying substance such as $CaCl_2$ granules, and layers of absorbent material, the gases entering by an inlet valve; the detector, into which the gases enter by a valve, comprizes a layer of pumice granules moistened with a mixt. of iodine pentoxide and fuming H_2SO_4, and a layer of cotton-wool, etc., for eliminating SO_2; and there may be a further layer of a weak absorbent for iodine, such an inactive charcoal or granules composed of alk. constituents and a binding medium, in order that the detector shall not respond to the small quantities of CO that may be passed when the respirator is first taken into use and also possibly to the traces passed continuously.

2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON AND EDWARD MACK

Icilio Guareschi. FELICE GARELLI. *Ann. accad. agr. Torino* **62**, 93–128(1919).—An obituary. ALBERT R. MERZ

Commemoration of Prof. Icilio Guareschi. ANON. *Giorn. farm. chim.* **69**, 57–81 (1920).—Biographical. A. W. DOX

Italo Giglioli. GIUSEPPE LO PRIORE. *Stas. sper. agrar. ital.* **53**, 332(1920).—An obituary. ALBERT R. MERZ

Precise values of the most important fundamental constants. J. J. VAN LAAR. *Chem. Weekblad* **18**, 397–400(1921).—Recognizing the desirability of greater accuracy in calcns. which the chemist and the physicist are called upon to perform, v. L. has tabulated a number of the more commonly used consts. The values which follow are those which in v. L.'s judgment are the best averages of previous detns. The acceleration of gravity (lat. 45), g = 980.616 cm./sec^2. If the mean density of the earth be taken as 5.52, the const. of gravitation. $f = 6.667 \times 10^{-8}$. The international atm. = 1033.23 g./cm^2. = 1.01320×10^6 dynes/cm^2. The velocity of light, $c = 2.999 \times 10^{10}$ cm./sec. The theoretical normal vol., v_V = 22417 cm.^{3} /g. mol. The at. wt. of H = 1.0077. The gas const., $R = 8.317 \times 10^7$ ergs./g. mol. = 82.09×10^{-3} l. atm. /g. mol. The cal. (15°) = 4.183×10^7 ergs, and hence 1 joule = 10^7 ergs =

0.2391 cal. Therefore, R = 1.988 cal. (15°)/g. mol. The charge of an electron, e = 4.774 × 10^{10} ± 0.004 (electrostatic units). The electro-chem. equiv. = 96460 coulombs / equiv. Avogadro's number, N = 0.6060 × 10^{24} mols./g. mol. Loschmidt's const. = 27.03 × 10^{18} mols./cc. The gas const. for 1 mol., k = 1.3725 × 10^{-16} ergs. The mass of the H atom = 1.663 × 10^{-24} g. The mass of an electron M_0 = 0.9005 × 10^{-27} g.; hence e/m_0 = 5.301 × 10^{17} electrostatic units. The Rydberg const. (for a material of infinite at. wt.), R_∞ = 109737.11 × c, from which Planck's const., h = 6.546 × 10^{-27} erg. sec. Furthermore, $\beta = h/k$ = 4.770 × 10^{-11} sec.; Wien's const., $c_2 = \beta c$ = 1.430 cm.; and the Stefan-Boltzmann const., σ = 5.738 × 10^{-5} g./sec.^{3}

L. H. Adams

Dimensional consideration on the basis of the law of equipartition. Ludwig Schiller. *Z. Physik* **5**, 159–62(1921).—The method of dimensions with temp. regarded as having the dimensions of energy and at. wt. of mass can be used to derive many known relations between physical consts. As new relations thus deduced S. gives: $\alpha\Sigma/\sigma$ = const. and $\alpha\Sigma A$ = const., where α = thermal expansion coeff., Σ = heat of fusion, σ = sp. heat, and A = at. wt.

F. C. Hoyt

Latent heat and surface energy—cohesion. Herbert Chatley. Shanghai. *Phil. Mag.* **42**, 183–4(1921).—A note on Hammick's paper (*C. A.* **14**, 682) pointing out that Bakker's formula used by H. is in direct contradiction to Mills' formula. The question of greater validity depends on exptl. support. A new expression of the van der Waals' pressure coeff. a is deduced by Chatley: $a = 2a_c\left(1 - \frac{T}{2T_c}\right)$ from Hammick's equation.

S. C. Lind

The critical energy increment and Trouton's rule. Eric K. Rideal. Univ. of Cambridge. *Phil. Mag.* **42**, 156–63(1921).—R. shows that the critical energy increment of activation of mols. is an av. value depending on the varying degrees of activation already possessed by the different mols. Hence, the wave length calcd. from the temp. coeff. may not have any direct significance and may not fall within the absorption region of the mol. The nature of the equil. between the mols. of any one species in their various stages of activation is assumed to follow the energy curves of the circumambient radiation. Only in the case of "black" mols. is the curve complete. At the critical temp. the max. number of mols. are activated for the reaction of condensation to a non-polymerized liquid. Since the latent heat of vaporization is given by the relationship $L = Nh\nu$, Trouton's const. is, on this hypothesis, an approx. expression of Wien's displacement law, $\lambda_{max.}\ T$ = const. The value of the const. calcd. from radiation data agrees closely with expt. A table is given showing L, the latent heat of vaporization calcd. from Wien's law, from van der Waals' expression, from Trouton's rule, and from exptl. data for a number of liquids or gases capable of liquefaction. For the simpler mols. the Wien displacement value agrees more closely with expt. For the more complex mols. the Wien displacement values agree remarkably closely with those calcd. from the van der Waals' relation, but are below the exptl. values which are in agreement with those calcd. by Trouton's rule. The divergence for the complex mols. is attributed to association. The extra energy supplied during vaporization is that required for dissociation and indicates in many cases a value $V_{vap.} = 2\ V_{diss.}$ A similar relation holds in many cases at the m. p. as is shown in a table for about a dozen substances.

S. C. Lind

The nature of chemical force and the anomaly of strong electroytes. William Hughes. Bedford, Eng. *Phil. Mag.* **42**, 134–8(1921).—To account for the anomaly of strong electrolytes in the application of the diln. law, H. assumes that the interionic forces in electrolytic solns. are inverse-square functions of the distances apart of oppositely charged ions, and that the forces causing dissociation of the electrolytes are in-

verse higher power functions of the distance. A quant. theoretical interpretation is given to the Rudolphi equation: $\frac{\alpha^2}{(1-\alpha)V^{1/2}} = K$, and a qual. one to the van't Hoff empirical relation $\frac{\alpha^{2/2}}{(1-\alpha)V^{1/2}} = \text{const.}$, in which α is the degree of dissociation, V the diln., and K the dissociation const. S. C. LIND

Theory of valence. I. The formulation of acids according to the law of non-polar atom-linking. HEINRICH REMY. *Z. anorg. allgem. Chem.* **116**, 255–66(1921).—R.'s summary is: "The law of Kossel (*C. A.* **10**, 2654) for the formation of polar compds. is generalized to a law for the formation of all chem. compds., which holds both for polar and non-polar (hetero-polar and homo-polar) atom-linkings. Especially non-polar atom-linkings seem to follow this law: If the valence-electrons, being under the influence of the valence-sphere of another atom, do not sep. themselves entirely from their own atom, they secondarily also have the tendency to form a group of their own, which is characterized by a max. of stability, within their original sphere. The validity of this law is proven by the fact that all known O-acids of elements preceeding the Al family, which are satd., from the point of view of coördinates, possess in their central group (Zentral Verein) a const. number of electrons, which is identical for nearly related elements. The number for O-acids of elements preceding Al is 6, and for all others it is 8; this is shown in a table contg. 37 O-acids and acid-ions. With this law of non-polar atom-linking the formulas for the "ortho-acids" of all acid-forming elements in a row preceding an element of the Al-family can be formulated without any auxiliary hypothesis, which is not possible with any of the other theories. The possibility of a physical interpretation of this electron-group is briefly discussed." E. FIERTZ

The variation of specific refraction of dissolved salts in dilute solutions. C. CHÉNEVEAU. *Compt. rend.* **172**, 1408–10(1921).—The specific refractive power of a dil. soln. remains const. down to a small limit of the equiv. concn. Assuming that the gas laws hold in dil. solns., and that the concn. of the dissolved substance is a function of the osmotic pressure, and taking into account the dissociation, the relation of the osmotic pressure to the sp. refraction was calcd. and shown in the form of curves for $Mg(NO_3)_2$, KCl, and NH_4NO_3. (Cf. *C. A.* **4**, 1710, 3034.) The change of sp. refraction with great increase of diln. is explained as possibly the variation of R, in the relationship $R = KN/(\nu_0^2 - \nu^2)$, with respect to the osmotic pressure of the dissolved substance, owing to the difference in the rate of change of the oscillation frequency of the atoms or molecules, ν_0, and their number, N, with increasing diln. E. P. WIGHTMAN

Some thoughts on the communication of M. Dubreuil. F. WALD. *Bull. soc. chim.* **29**, 266–71(1921); cf. Dubreuil, *C. A.* **15**, 196.—Wald claims to have presented, in reverse form, the ideas in Dubreuil's paper, "*The calculation of the number of independent components in a system*," as early as 1897. By arranging in a rectangular table the numbers of radicals concerned in a chem. equation so that each column represents a mol. of one of the compds. concerned and each line contains only one kind of radical, and using the principal of determinants, the value and sign of the valence of each radical can be deduced. With the assumptions (*a*) that one class of substances (elements) cannot interact without producing substances of another class, (*b*) that reactions of members of this class of substances to form a single resultant substance shall be represented by "fundamental" equations, (*c*) that all other reactions be represented by "secondary" equations, (*d*) that original substances be considered positive and resultant substances negative, Wald states that he can work out an analytical theory of chemistry instead of the present synthetic one. The process is from less pure to more pure compds. and finally to elements. F. E. BROWN

Number of atoms and the physical behavior of organic liquids. W. HERZ. *Z. anorg. allgem. Chem.* **116**, 250–4(1921).—Based on the formula of Groshans $n = \frac{193.M^2}{T_s^2.d_s}$ (*Ann. Physik* [4] **61**, 142(1898)), where n = number of atoms in the mol., M = the mol. wt., T_s = b. p. in abs. temp. and d_s = density at b. p., and a number of other relations found by Herz and others (*C. A.* **14**, 682), the following formulas are derived and discussed. They all agree fairly well with the empirical data: $M/T_s^2 = 0.00077 = \frac{1}{16.2.R}$; $V_k = \frac{0.1737.M^2}{T_s^2 d_s}$ (V_k = critical vol.); $V_k = 1.34.10^{-4}.\frac{M}{d_s}$; $s.M = 2.44.\frac{T_k}{p_k}$ (s = sp. heat: T_k = critical temp.; p_k = critical pressure). E. FIERTZ

Allotropic varieties of oxides. MLLE. S. VEIL. *Compt. rend.* **172**, 1405–7(1921); cf. *C. A.* **14**, 2311.—A study of the elec. cond. of a number of metallic oxides, as a function of their temp., shows that as a rule cond. is an increasing function of temp., the curve having a parabolic direction. Certain oxides, *e. g.*, Fe_3O_4 and CdO, show maxima and minima in their curves, which are attributed to allotropic variations. The curves for Fe_3O_4 and CdO are given. E. P. WIGHTMAN

Water and ice. GERVAISE LEBAS. *Chem. News* **122**, 249–50(1921).—Phenomena are cited which, in LeB.'s opinion, exclude full quadrivalent function for O in these mols. It is suggested that the O_2 mols. may be sepd. from each other by a shell of dielectric and the valencies are activated but exerted only very loosely, resulting in various degrees of association. A. R. M.

Viscosity of water at low rates of shear. A. GRIFFITHS AND (MRS.) CONSTANCE H. GRIFFITHS. *Proc. Phys. Soc.* (London) **33**, 231–42(1921); cf. *C. A.* **10**, 1956.—The detn. of the coeffs. of viscosity of H_2O by a method in which the H_2O is forced along glass capillary tubes of about 1.5 to 2.0 mm. bore at rates of flow varying from one l. in 2 yrs. to one l. in 24 yrs. The liquid fills a closed tubular circuit composed of two long horizontal tubes and 2 shorter vertical ones. The circulation is caused by a difference of d. between the liquids in the 2 vertical tubes, that in one being pure H_2O and that in the other a weak soln. of uranine. In the final form of the app. the 2 vertical tubes were brought close together so that they could be kept at the same temp. in order to eliminate corrections for temp. differences. The value of the coeff. of viscosity at 18° was found to be 0.010624 ± 0.000229 (assuming observations of equal wt.) and 0.010569 g. per cm. sec. from Hosking's formula. Thus there is no exptl. evidence that at the extremely low rates of shear (0.0017 to 0.0233 radians per sec.) the viscosity of air-free H_2O in glass capillary tubes differs from its value at normal rates of shear (5,000 to 10,000 radians per sec.). C. C. VAN VOORHIS

Properties of carbonic acid. J. H. WEST. *Chem. Trade J.* **69**, 4–5(1921).—Graphs of the physical properties of CO_2 are given, including the vapor pressure, sp. heat, solv. in water, latent heat of vaporization and sp. gr. of liquid and satd. vapor. H. BUTTLER

The vapor tension of hydrogen sulfide. E. CARDOSO. Univ. Naples. *Gazz. chim. ital.* **51**, I, 153–64(1921).—Some years ago C. (*C. A.* **7**, 3866, 3867) learned that the prepn. of chemically and thermodynamically pure H_2S is difficult. The H_2S then used was prepd. with pure FeS and HCl and after liquefaction and distn. 14 times failed to give satisfactory results for the critical point owing to the H_2 that could not be removed. Since accurate data on the vapor tension of H_2S were required by C. and those given in the literature are quite old he has detd. them again. H_2 was removed by passing the H_2S through NaOH and then liberating the H_2S again with acid but the

distn. gave a larger residue of the liquid with a higher b. p. than before. The method finally adopted follows: 50 g. $Mg(OH)_2$ were placed in a 1 l. flask with 0.75 l. H_2O and treated with H_2S with agitation until it was no longer absorbed. The mixt. was then heated and the pure H_2S evolved was collected and liquefied by cooling with liquid air. The H_2O was removed with a good condenser and then with a U tube contg. P_2O_5. This H_2S also contained the high-boiling residue. C. observed when tubes in which liquid H_2S had been kept were emptied that drops of this high-boiling residue could be found sticking to the wall of the tube, indicating that this impurity is little sol. in liquid H_2S. Bulbs contg. a constriction in the middle and at one end were prepd. The H_2S was liquefied in the lower bulb and the upper constriction was sealed off. The whole was then immersed in a cryostat at −80° conveniently made of a Dewar flask half full of petroleum ether to which liquid air was added at such a rate as maintained this temp. After 1.5 hrs. in this bath the tube was quickly removed, turned over in order to transfer the liquid into the upper empty bulb and placed in the bath again. The bulb contg. the drops adhering to the wall was now sealed off. This treatment diminishes the soly. and removes the high-boiling residue before fractionation. After a careful consideration of all the facts C. concludes that this insol. residue is composed of hydrogen polysulfides. This if true explains why H_2S gas under pressure decreases in vol. since in accordance with Le Chatelier's principle this could be expected to occur with the formation of H_2S_x. The app. used for the vapor tension detns. was previously described. The detns. were made from 0° to 100.4° (the critical temp. of H_2S). Detns. were made at 16 points and full details are given. Enough data to construct the curve roughly will be given here: 0° 10.20 atms.; 10°, 11.68 atms.; 20°, 17.24 atms.; 30°, 22.00 atms.; 40°, 27.80 atms.; 50°, 34.53 atms.; 60°, 42.22 atms.; 70°, 51.24 atms.; 80°, 61.88 atms.; 90°, 74.17 atms.; 100°, 88.32 atms.; 100.4°, 88.92 atms. The data agree only moderately well with those of earlier workers owing probably to their inability to remove the impurities effectively. E. J. WITZEMANN

Coefficient of diffusion of certain saturated solutions. B. W. CLACK. *Proc. Phys. Soc.* (London) **33**, 259–65(1921).—This paper gives an account of expts. on the diffusivity of satd. solns. of KCl, NaCl and KNO_3 at const. temps. near 18° when the steady state of diffusion has been attained, employing a method similar to that previously used by C. (cf. *C. A.* **4**, 400; **9**, 1416; **11**, 2986). The soln. under investigation is maintained at complete satn. by the presence of salt crystals in the diffusion vessel. The theory given takes into account the change in vol. of this salt as it dissolves, and an expression is obtained for the coeff. of diffusion at complete satn., which depends on the rate of change in wt. of the diffusion vessel with time. The exptl. results agree closely with values extrapolated from results previously found for less concd. solns. The values obtained for the coeffs. of diffusion of satd. solns. of the salts mentioned are: 2.107×10^{-5} c. g. s. for KCl at 17.3°; 1.522×10^{-5} for NaCl at 17.1°; and 1.171×10^{-5} for KNO_3 at 18.1°. C. C. VAN VOORHIS

The influence of the water content on the absorption by active charcoals. HEINRICH HERBST. *Biochem. Z.* **118**, 103–19(1921).—Charcoal can take up to 50% of its wt. in H_2O and still give the appearance of being dry. Such an absorption of H_2O is due to capillary forces and decreases to a marked degree the pure absorptive power of the charcoal for gases. This is shown in tables for chloropicrin, phosgene, Cl and HCN. With dry charcoal as a standard it was found that the technical products yield only about 50% of their potential absorptive value. In addition to this pure absorption capacity of charcoal there is a catalytic adsorption reaction power of great significance. This increases with the increase in H_2O content. When about 10 to 12% H_2O is present in the charcoal as prepd. for the mask this % is increased by the moisture of the breath and reaches the optimum of 22 to 30%. It is, therefore, concluded that an initial H_2O

content of 10% does but little harm, since the hydrocatalytic action of many substances which have but a slight absorption constant can oppose the H_2O effect.

F. S. HAMMETT

Estimation of the adsorbing power of charcoal. I. M. KOLTHOFF. Utrecht. *Pharm. Weekblad* 58, 630–56(1921).—In general, Freundlich's rule (that different varieties of charcoal show the same order of adsorbing power for different substances) is valid. There are exceptions, and there is no theoretical proof of the rule; but it serves fairly well as a guide. The order of adsorbing power is: Merck's blood charcoal > vegetable carbon = medicinal carbon > bactanate > norite. Vegetable and medicinal carbon are only approx. equal; each is slightly better than the other for certain substances. It is difficult to choose a suitable standard substance for evaluating the adsorbing power of charcoals. The simplest is I; but it does not follow the adsorption isotherm. Dyes are not suitable because their purity and strength are too uncertain. Alkaloids and heavy metals are adsorbed in too small amts. to serve as standards. Formalin meets all the requirements except that the amt. adsorbed is small. The best available choices seem to be $HgCl_2$, $Hg(CN)_2$ and PhOH. It is sufficient to require that 1 g. of the charcoal, shaken with 100 cc. of 0.1 *N* soln. of the standard, shall adsorb a certain minimum amt. It is not necessary to det. the entire adsorption isotherm. Data for the above varieties of charcoal are given showing the adsorption of I, PhOH, $HgCl_2$, $Hg(CN)_2$, As_2O_3, $CuSO_4$, salicylic acid, methylene blue, crystal ponceau, morphine, quinine, strychnine and 5 other alkaloids. JULIAN F. SMITH

Some factors governing the sorptive capacity of charcoal. Sorption of ammonia by coconut charcoal. JAMES B. FIRTH. *J. Chem. Soc.* 119, 926–31(1921).—Coconut charcoal carbonized at as low a temp. as possible and then heated to 600° exhibits considerable increase in sorptive power without material increase in density. At 900° a much greater increase is obtained coincident with a marked increase in density; but increased density does not always mean increased activity. Activity of the charcoal deteriorates with time. A graph is given showing equil. pressures at 18°, 0°, and −20°. JEROME ALEXANDER

The absorption of carbon monoxide contained in a current of air. A. DESGREZ. H. GUILLEMARD, A. HEMMERDINGER, AND A. LABAT. *Chimie & industrie* 6, 118–23 (1921).—For the absorption of CO contained in a current of air having a certain velocity, the ordinary reagents are inefficient as the rate of absorption is too low. This is especially noticeable in the case of chromic acid, $KMnO_4$, alk. peroxides, and I_2O_5. Under the same conditions charcoal possesses a certain absorptive power, which is appreciable only for low CO contents. Platinized asbestos catalyzes the reaction even at ordinary temps.; but a rise in temp. greatly accelerates the reaction and becomes absolutely necessary if small amts. of platinized asbestos are used. The rate of absorption by I_2O_5, which is too low even at 50°, is greatly increased by the addition of small amts. of H_2SO_4. Max. efficiency is obtained with fuming acid containing 10% SO_3. Under these conditions I_2O_5 can be replaced by HIO_4; but in this case with an equal wt. of reagent the absorbing mixt. is exhausted more rapidly. The app. used and the method of carrying out the tests are described in detail. A. P.-C.

Contribution to the stoichiometry of adsorption. I. Adsorption of cations of the alkalies and alkaline earths. SVEN ODEN AND HUGO ANDERSSON. *J. Phys. Chem.* 25, 311–31(1921).—Using a Zeiss interferometer to measure the change in concn. of solns. of the alkali and alk. earth nitrates after shaking with charcoal, the amts. adsorbed by the charcoal were detd. It was established clearly that the amt. of the salt adsorbed in each case was greater as the at. wt. of the cation increased. An attempt was made to express the adsorbed quantity as a function of the remaining concn. by means of the Freundlich formula $y = Kc^{\beta}$. It was seen, however, from data obtained, that if the

coeff. K and the exponent β are calcd. from values obtained at low concns., the agreement at higher concns. is not good, and *vice-versa*. Furthermore, it was observed that if the charcoal is carefully purified, equal amts. of anions and cations are adsorbed. If this were proved not to be the case, as H. Lachs and L. Michaelis and other authors have maintained, the soln. after adsorption should, by hydrolysis, have either an acid or an alk. reaction. No such reaction could be discovered in any case, either with sensitive indicators or with the H electrode. These expts. make it very probable that the so-called decompn. by adsorption is only apparent, the cause being adsorbed impurities (H or OH ions) which are partially thrown out by the adsorbed soln. A striking fact in the experiences of other authors, who hold the contrary opinion concerning unequal adsorption of anions and cations, is that those adsorbents which are said to adsorb the base and set the acid free are derived from acid solns. or have been treated with acids, whereas the adsorbents which appear to adsorb the acid and set the base free are prepd. from alk. solns. This can hardly be due to chance only, but depends on the circumstance that the disintegrated constituent which is said to be set free is in reality retained as traces of acid or base, not washed out, and not detected until thrown out by the addition of the neutral salt soln. Michaelis in a later paper has admitted errors in his early method and has found that cation and anion are adsorbed in precisely equiv. amts. J. T. R.

Preparation of dispersed substances in gaseous media. V. KOHLSCHÜTTER AND J. L. TÜSCHER. Univ. Berne. *Z. Elektrochem.* **27**, 225–56(1921).—The production of dispersed substances in gaseous media and their methods of prepn. are discussed, with special reference to metallic oxides. The general scheme employed in the present investigation consists in making the metal one electrode of an arc, and oxidizing its vapor by means of a current of air. A detailed diagram is given showing the app. employed. The separation of the oxide from the vapors or fumes is brought about by pptn. in an elec. corona discharge. The sp. behavior of the various fumes, with regard to facility and completeness of pptn., depends on factors associated with the nature of the substance and the form of the fume particles. The fume production dets. the state of subdivision of the dispersed product, and the elec. conditions in the pptn. cell its mass-form; but both of these depend in a measure on the nature of the substance. Dispersed oxides of the following metals have been prepd.: Bi, Pb, Cu, Ni, Fe, Mn, Cr, Ag, Cd, Zn, Sb, As, Sn, Al, Ca, Mg, and Si; and mixed oxides have been formed by using electrodes consisting of the following combinations of elements: FeSi, FeAl, FeCr, FeB, FeV, FeTi, FeMo, CuSi, CuMn, NiAl, NiSi, TiSi, MnSn, CuFe and MnB. The various products obtained have been described. The size of the dispersed particles corresponds with the upper limit of the colloidal state. H. JERMAIN CREIGHTON

An explanation of Liesegang's rings. HUGH MCGUIGAN. Univ. of Illinois. *Science* **54**, 78–80(1921).—When a minute droplet of $AgNO_3$ soln. is placed on a gelatin gel containing $K_2Cr_2O_7$, there is an immediate formation of a circle of Ag_2CrO_4 about which is a sharply demarcated zone of influence from which the chromate has been removed. The Liesegang ring formation when a larger drop of $AgNO_3$ is used is explained as follows: "Ag_2CrO_4 is formed and a clear zone results in the gelatin by the attraction of the chromate to the silver. Beyond this zone of influence, the chromate is fixed and remains so unless an attraction force is exerted. The $AgNO_3$ now wanders on through the ring into the clear zone until it approximates the chromate gelatin sufficiently close to exert an attraction which again draws the chromate and forms another ring and clear zone. At the same time the chromate exerts a pull on the silver and the ring is formed where the forces are balanced. Again it may be presumed that to start the chromate moving will require a greater force than to keep it moving after the start is made; consequently the second ring is sepd. from the first. With each succeeding ring the concn. of the silver is less and this also will operate to remove the succeeding

rings farther apart." As a requisite for ring formation the ppt. formed must be permeable to the liquid soln. used, in this case $AgNO_3$. F. L. BROWNE

A simple apparatus for determining the coagulation velocity of gold sols. EMIL HATSCHEK. *Trans. Faraday Soc.* (adv. copy) **1921**, 2 pp.; 3 illus.—The app. is a rectangular cell, the two sides of which are glass plates, while the ends and bottom are of ebonite or other inert opaque material. This is divided by an oblique glass partition. One-half of the cell is filled with the red sol to be examd. and the other with the completely coagulated blue sol. This cell is placed between two guides mounted on a base plate and a second cell exactly like it is placed immediately on top of it. This cell does not require a partition except for the purpose of providing the same optical thickness. The sol which is to be examd. is mixed with a known vol. of electrolyte—the time of adding being noted—in a beaker and then charged into the upper cell. The fields of which one varies from 100% red to 100% blue and the other slowly changes from red to blue, are matched through a slit cut in a black screen, and the % blue read off on a scale on the base plate. Best results were obtained in diffuse daylight. The results agree with the results Zsigmondy obtained in testing v. Smoluchowski's formula. Comparison is made with the results obtained by Paine in the coagulation of $Cu(OH)_2$. H. B.

The colloidal system of silica-alumina. J. SPLICHAL. *Chem. Listy* **15**, 53–6, 88–90, 110–13, 140–3, 164–7(1921).—The following observations were noted during the expts.: The hydrosols, silica and alumina, ppt. each other. Even if the colloidal particles at certain conditions of concn. fail to ppt. and settle out, then the viscosity and the opalescence of the mixt. of hydrosols are to be considered as evidence of the beginning of coagulation in the system. The opalescence is caused by the dispersion phase, which seps. first in a solid form. In these cases the solid phase always remains dispersed, does not settle out and its quantity is not increased with time. In the same manner Freundlich (cf. Ishizaka, *C. A.* **7**, 2878) and Paine (*Kolloid. chem. Beihefte* **4**, 24(1912–3)) found that in order to obtain a measurable coagulation in simple hydrosols, the added electrolyte must be present in a certain definite concn. The pptn. is due only to the reciprocal action of the hydrosol particles. The electrolyte, present in the hydrosols in very small concns., has no effect on the pptn.; the viscosity is decreased. The pptn. is most rapid and the viscosity is greatest in a hydrosol mixt. in which the concn. ratio of Al_2O_3 to SiO_2 is 1:3. The prepn. of the alumina hydrosol from com. Al acetate according to the procedure of Crum (*Ann.* **89**, 156(1854); *J. prakt. Chem.* **61**, 90(1854)) did not prove successful owing to the presence of small amts. of H_2SO_4 in the Al acetate. H_2SO_4, even in very small amts., coagulated the alumina hydrosol. To avoid this, S. prepd. the Al acetate by the action of pure $C_2H_4O_2$ on pure Al. The excess of $C_2H_4O_2$ was removed by steam distn. JOHN M. KRNO

The stability and reversibility of the transformations of hydrosols obtained by the hydrolysis of salts. A. TIAN. *Compt. rend.* **172**, 1402–4(1921).—Although the hydrosols of metallic hydrates are in general not very stable, it is exceptional to see the saline solns. of the heavy metals, which contain, owing to hydrolysis, a greater or less proportion of their base in colloidal suspension, flocculate. This is explained on the ground that while the particles of the hydrosol tend to unite to form particles of greater size, this process is also reversible owing to chemical forces tending to increase dispersity, so that an equil. is established. E. P. WIGHTMAN

A colloid theory of the corrosion and passivity of iron, and of the oxidation of ferrous salts. JOHN A. N. FRIEND. *J. Chem. Soc.* **119**, 932–49(1921).—Expts. are detailed showing that rapidly moving water does not rust Fe even in the presence of dissolved air. This, together with the fact that in general higher purity means diminished reactivity, is held to indicate that the moving water "sweeps away from the surface of the metal

some catalyst which assists the metal to corrode, and in the absence of which the metal simply dissolves in the liquid ionically with such small velocity that it is almost 'passive.' This catalyst must be derived from the Fe, and F. believes it to be the hydrosol of iron hydroxide. It is suggested that: (1) Fe is noble or "passive" towards distd. water in the absence of a catalyst and dissolves very slowly only because traces of electrolytes are present; (2) the dissolved Fe, probably at first present in ionized ferrous state, is soon converted into the sol of ferrous hydroxide; (3) this sol is oxidized by dissolved O to the sol of a higher hydroxide, $Fe(OH)_3$ sol being formed if sufficient O is present, or ferroso-ferric hydroxide sol if the O supply is limited; (4) the higher hydroxide sol now acts catalytically, oxidizing the metallic iron rapidly and simultaneously being reduced to the lower hydroxide sol which is again reoxidized as dissolved O diffuses toward it. Consequently anything affecting sol formation should influence corrosion. Exptl. results are given showing that the action of dissolved electrolytes bears a striking resemblance to the results obtained by Hardy, Freundlich, and Linder and Picton on the pptg. effects of salts on $Fe(OH)_3$ hydrosol, and are regarded by F. as strongly supporting his theory. Protective colloids which exert a retarding action on the catalytic activity of suspensoid colloids also tend to inhibit corrosion, though their protection factors do not parallel their Zsigmondy gold numbers. F. gives possible reasons for this discrepancy. Whitney's view that alkalies act by depressing ionization is controverted by the fact that dil. alkali carbonates accelerate corrosion. This anomaly does not apply to the colloid theory, for there corrosion stops only when the alkali is concd. enough to ppt. the catalytic sol as rapidly as it is formed. Alc. which dehydrates the sol decreases corrosion even in concns. which show greater O soly. Salts of org. acids, catalyst " poisons," temp. changes, radioactivity, and passivity all show phenomena harmonizing with the colloid theory of corrosion. In fact similar autocolloidal catalytic explanations might account for numerous other reactions. [No mention is made of W. H. Walker's electrolytic theory. ABSTR.] JEROME ALEXANDER

A new theory of the corrosion of iron. J. NEWTON FRIEND. *Trans. Am. Electrochem. Soc.* **40**, 13 pp. preprint(1921); 9 illus.—See preceding abstr. F. H. HOTCHKISS

The color of photochloride and of colloidal silver. I. K. SCHAUM AND H. LANG. Giessen. *Kolloid-Z.* **28**, 245–9(1921).—The purpose of these studies is to observe the relation between the color of the photohalide and the colloidal character of the Ag particles adsorbed by the Ag halide. The effect is shown of increasing and decreasing the size of the particles of a Ag sol upon the color of the sol in transmitted and reflected light and in the light scattered by the individual particles (observed under the ultramicroscope). Very uniformly homodispersed and easily reproducible Ag sols were made by "developing" a soln. of $AgNO_3$ and Na_2SO_3 with a soln. of *p*-phenylenediamine and Na_2SO_3 in the presence of gelatin and of a "nucleus" Ag sol. The final size of the particles depends upon the concn. of the nucleus sol. The nucleus sol was made by Carey Lea's dextrin method, and had a very high dispersity. On the basis of Mie's theory of turbid media Müller has shown (*C. A.* **5**, 3368) that as the diam. of the particles changes from 80 to 180 $\mu\mu$ the color in transmitted light changes in the order: orange–red–purple–violet–blue–blue green. With decreasing dispersity the authors find the order: orange–red–purple–blue violet–blue green. The color in reflected light is complementary except in the coarser dispersions where the turbidity of the sols affects the observations. If the size of the particles is decreased by adding agents to dissolve the Ag, such as photographic reducers, H_2O_2, etc., the color does not pass back along this scale, but remains unchanged in shade, merely diminishing in intensity until it vanishes. By means of the ultra-microscope the color of the light scattered by the individual particles as they increased or decreased in size was observed. By allowing $AgNO_3$ to diffuse slowly into a thin layer of gelatin gel contg. the nucleus sol and the reducing agent, on the object

glass of the ultramicroscope, the changes in color with change in size of a single particle could be readily followed. Theory predicts the color change: violet–blue–green–yellow–orange–red. The changes observed as the particles increased in size were: blue violet–blue–blue green–orange–yellow–white. In a field contg. numerous green particles, there were often found some red particles. This is attributed to a physiol. effect because (1) red particles were observed only in the presence of numerous green ones; (2) when a red particle was isolated by using a diaphragm in the ocular the color was faint and appeared differently to different observers; (3) if a coarse dispersed sol was observed in bright-ground illumination with green light and immediately thereafter in dark-ground illumination using white light, all particles appeared red until the eye was rested, when they appeared white). With decreasing size of particle, *i. e.*, when persulfate or Farmer's reducing soln. was allowed to diffuse into the gel, the color did not shift back along the scale, but merely decreased in intensity until the particle vanished. Spectrophotometric examn. showed that the highly dispersed sols have an absorption max. in the ultraviolet which shifts into regions of greater wave length as the dispersity decreases. The coarser dispersions have a tendency to show several max. F. L. Browne

A colloid chemical study of the action of nuclei. F. Sekera. Vienna. *Kolloid-Z.* **28**, 254–8(1921).—The study of the action of nuclei in causing crystn. of supersatd. solns. gives an opportunity for examg. the boundary region between molecular and colloidal dispersions. In concd. solns. the solute mols. unite to form complexes which become larger as the concn. increases. The author assumes that these complexes may be treated as a colloidally dispersed phase of very high dispersity. Since the soln. pressure of a substance increases greatly with increase in convexity of the interface, the soly. of small particles increases with their dispersity. A supersatd. soln. is therefore a *stable* condition of equil. between a soln. and a very highly dispersed second phase consisting of these mol. complexes. Crystn. can be induced in 2 ways: (1) by introducing a nucleus consisting of a crystal of the solute (the nucleus being less highly dispersed than the mol. complexes it is less sol. and grows at their expense); and (2) by inducing local changes in concn. and hence in size of the mol. complexes, in which case the larger complexes act as crystn. nuclei. Such local change in concn. may be caused, for example, by differences in adsorption at an irregularity in the walls of the containing vessel. Undercooled melts are regarded similarly as dispersed systems of mol. complexes in a dispersion medium of simple mols. The m. p. is a function of the dispersity. F. L. Browne

Colloidal arsenates. II. Cadmium arsenate jellies. G. Klemp and J. v. Gyulay. Budapest. *Kolloid-Z.* **28**, 262–8(1921); cf. *C. A.* **12**, 2151.—A completely transparent gel is formed when a soln. of a Cd salt is mixed with a soln. of KH_2AsO_4 of suitable concn. The KH_2AsO_4 may be replaced by a soln. of Na_2AsO_4 previously neutralized with $HC_2H_3O_2$, HCl, or H_3AsO_3. After a short time the gel becomes opalescent and finally breaks up, depositing crystals of cadmium arsenate. Photomicrographs of the crystals formed under varying conditions are given. By analysis, the compn. of the crystals was found to be $2Cd_3(AsO_4)_2.4CdHAsO_4.9H_2O$. F. L. Browne

The phenomena of coagulation in gelatin-sodium chloride solutions. W. Moeller. Hamburg. *Kolloid-Z.* **28**, 281–90(1921).—Two % gelatin solns., satd. with NaCl, were mixed with solns. of HCl or of $HC_2H_3O_2$, also satd. with NaCl. Part of the gelatin was thrown down as a coagulum resembling that of blood fibrin. After varying lengths of time, this was filtered off and the amt. of gelatin and of acid remaining in the filtrate detd. There is an optimum concn. of acid for max. coagulation of the gelatin. About 90% is coagulated in 0.05 *N* HCl and 84% in 0.1 *N* $HC_2H_3O_2$. Part of the acid is adsorbed by the coagulum. F. L. Browne

The velocity of coagulation of Congo rubin hydrosols in the presence of urea and

cane sugar. JOSEF REITSTÖTTER. *Kolloid-Z.* **28**, 268–9(1921). Lüers (*C. A.* **15**, 788) found that the velocity of coagulation of Congo rubin hydrosols is in accord with Smoluchowski's theory of coagulation (*C. A.* **11**, 3140). The author extends this work by observing the influence of a change in the viscosity of the medium by addition of urea or cane sugar. The decrease in the velocity of coagulation with 0.18 *N* NaCl by the presence of these substances is greater than the theory predicts from the change produced in the viscosity. F. L. BROWNE

The influence of dyes on the electrocapillary curve. H. FREUNDLICH AND MARIE WREschner. Kaiser-Wilh. Inst., Dahlen. *Kolloid-Z.* **28**, 250–3(1921).—According to the theory of Freundlich and Rona (*C. A.* **15**, 1447) one must distinguish between two sorts of p. d. at the interface between a metal and a soln. The Nernst p. d., ϵ, depends upon the concn. of the metal ions in the skin of soln. on the metal surface. The e. m. f. of a galvanic cell depends upon this p. d. The electrokinetic p. d., ζ, is the p. d. between the layer of soln. held fast on the metal surface and the movable layer within the body of the soln. and depends upon the concns. of all ions present, particularly the readily adsorbed and polyvalent ions. Electrokinetic phenomena such as kataphoresis depend upon ζ. The electrocapillary curve of a capillary electrometer depends upon both ϵ and ζ. Strongly adsorbed basic and acid dyes are suitable for testing the theory. The e. m. f. of the cell $Hg|0.5\ N\ KCl|KNO_3$ soln.$|AgNO_3$ soln.$|Ag$ was found to be 462 m. v. Addition of the basic dye methyl green or methylene blue or the acid dye sodium alizarinsulfonate to the KCl soln. left the e. m. f. unaltered. The electrocapillary curve in 0.5 *N* KCl soln. was measured in a capillary electrometer before and after the addition of these dyes. The max. of the curve was lowered and shifted toward the positive side by the basic dyes and toward the negative side by the acid dye, in agreement with the theory. F. L. BROWNE

The microscopic forms of iron rust. ADOLF ACKERMANN. *Kolloid-Z.* **28**, 270–80 (1921).—During the rusting of iron in the presence of a minimum of H_2O the rust appears in peculiarly shaped protuberances. Small particles of Fe were placed on an object slide and a very small drop of dil. acid soln. placed near by, the whole being covered by a cover glass cemented in place. The rusting of the Fe in the moist atm. contg. acid vapors was observed under the microscope. Microscopic droplets gathered on and about the Fe particles in a regular manner and rusting proceeded where they touched the Fe. The gel of $Fe(OH)_2$ formed first and became oxidized more or less rapidly to $Fe(OH)_3$. The rust appeared in remarkably regular outgrowths from the Fe particles. These sometimes consisted of chains of spherical droplets, sometimes of cylindrical stalks ending in large bulbs or in brush-like protuberances, and frequently of long threads which often curved around to join the Fe particle at a second place. These forms were composed of a solid outer membrane which was sometimes hollow, and sometimes filled with a gelatinous liquid. In the latter case the forms were very sensitive to temp. changes which caused them to twist about and break up into spherical drops. These drops showed a striking resemblance to living organisms in that they enclosed within a semipermeable membrane or cell wall, a gelatinous fluid and a vacuole or nucleus. Frequently large drops became subdivided by cross walls or membranes, a process resembling cell division. The similarity in shape of many of the forms to the iron bacteria is pointed out. "The observations made so far are not comprehensive enough to det. whether these similarities are merely superficial or whether they have a deeper and more far-reaching relation to vital processes." Numerous drawings and photomicrographs are given. F. L. BROWNE

The solubility of calcium sulfide in the presence of hydrogen sulfide. E. H. RIESENFELD AND H. FELD. *Z. anorg. allgem. Chem.* **116**, 213–27(1921).—In an atm. of H_2S CaS forms $Ca(SH)_2$, which is much more sol. than CaS. At 20° the soly. of

CaS in pure water is 0.212 g. CaS in 1000 cc.; under the H_2S-pressure of 760 mm. Hg, the soly. is 206.5 g. CaS in 1000 cc. at 20°. For high pressures of H_2S (200–760 mm.) the soly. can be represented by the formula $c_1 = K_1 + K_2.p$ in which c_1 = g. $Ca(SH)_2$ in 100 cc. and p = pressure. For 20°: $K_1 = 25.17$; $K_2 = 0.00696$. For 0°: $K_1 = 28.65$; $K_2 = 0.00499$. For 40°: $K_1 = 23.10$; $K_2 = 0.00708$. The empiric formula $c_2 = \sqrt{K_3}.\log p$ covers all pressures from 0 to 760 mm. Hg. For 20° $K_3 = 0.1094$. By allowing a $Ca(SH)_2$ soln. to stand under vacuum for several days, very *pure CaS* could be prepd. E. FIERTZ

The determination of the rate of solution of atmospheric nitrogen and oxygen by water. III. The rate of solution of air by quiescent waters under laboratory conditions. W. E. ADENEY AND H. G. BECKER. Roy. Coll. Sci., Ireland. *Phil. Mag.* **42**, 87–96 (1921).—There are three cases for the solution of a gas in a liquid: (1) rapid mixing, (2) no mixing, (3) slow or imperfect mixing. The first case has already been treated in former papers (*C. A.* **14**, 8, 491, 1920). The second case never occurs naturally and probably cannot be realized under laboratory conditions. The third case is treated in the present paper. The rate of soln. is expressed by $dw/dt = a - bw$ where $a = SAp$ and $b = f(A/V)$, w is the total quantity of gas in soln. at any moment, S is the initial rate of soln. per unit area, A is the area of surface, p is the gas pressure, f is the coeff. of escape from the liquid per unit area and vol. and V = vol. of liquid. Aeration was carried out in tap water and in sea water at 15°. The values of b were for tap water: 0.0186; and for sea water: 0.0250, for the exptl. condition obtaining. Correcting for surface and vol. $f = 0.388$ for tap water, and 0.509 for sea water. Expts. in a vessel 1800 mm. deep and 18 to 24 mm. cross section showed that mixing induced by surface evapn. takes place to the depth of 1800 mm. and is more rapid for sea water than for tap water. An expt. in a tube 300 mm. long with bulb of 175 cc. capacity near each end connected by a tube 6.4 mm. bore showed that the concd. layers of salt solns. stream downward with little or no lateral dissipation of their air content in the upper bulb. Sea water when satd. with air at 13° contains per l. 6.06 cc. O_2 and 11.77 cc. N_2. S. C. LIND

The correlation of compound formation, ionization and solubility in solutions. Outline of a modified ionization theory. JAMES KENDALL. *Proc. Nat. Acad. Sci.* **7**, 56–62(1921).—In view of the fact that satisfactory agreement with the Ostwald diln. law has been definitely established only for 2 restricted types of electrolytes, weak acids and bases, in a single solvent, water, and even then through a limited concn. range of dilns. greater than $N/16$, and numerous attempts at reconciliation having failed, the tendency is now widespread either to deny the applicability of the law of mass action to the ionization of strong electrolytes or to modify the ionization equation itself. On the basis of exptl. work performed by K. and collaborators during the past 7 years, a modification of the current ionization theory has been proposed, under the assumption that "ionization is preceded by combination between solvent and solute, and is, indeed, a consequence of such combination." According to this view, ionization in solns. is due not to solute alone, nor to solvent alone, but to combination between the two to form unstable complexes. Instead of a simple equil. such as $KCl \rightleftharpoons K^+ + Cl^-$ for a univalent electrolyte in aq. soln., one now has to consider a complicated series of equilibria between many different mol. and ionic types, such as $(KCl)_x$; $(KCl)_x(H_2O)_y$; $[(KCl)_xCl]^-$; $[(H_2O)_yCl]^-$; etc. There is also an apparent relation between degree of ionization of an electrolyte and its power to form hydrates. It is a very striking fact that with mercuric salts, the one series in which ionization varies considerably, all of the highly ionized salts yield hydrates. The further development of this topic and the presentation of quant. results will be given in forthcoming articles in the *J. Am. Chem. Soc.*

J. T. R. ANDREWS

A theory explaining the slow hydrolysis of certain salts. A. TIAN. *Compt. rend.*

172, 1179–81(1921).—T. notes that, in all cases where hydrolytic equil. is established slowly, one of the products tends to be present in a colloidal state. Hydrolysis will be retarded by two reactions, the ionic reverse of the hydrolysis taking place in the aq. phase, and the reaction between the sol. product of the hydrolysis and the colloid. This latter will be slower as the colloidal particles grow larger, furnishing less surface per unit mass. The total rate of hydrolysis will, then, depend on the rate of growth of the colloidal particles. T. shows that the rate is slowed by gelation where particles are given less chance to grow, and also that the addition of an excess of colloid retards the reaction. A. E. Stearn

Velocity of reaction in mixed solvents. I. The velocity of saponification of two ethyl esters in ethyl alcohol-water mixtures. Albert E. Cashmore, Hamilton McCombie and Harold A. Scarborough. Univ. Cambridge. *J. Chem. Soc.* **119,** 970–8(1921); cf. *C. A.* **9,** 1466.—The sapon. of BzOEt and iso-$PrCO_2Et$ in EtOH-H_2O mixt. has been studied. The reaction is bimol. and the value of the velocity const. is independent of the initial concn. of the ester or of the alkali. The ratio of k for iso-$PrCO_2Et$ to that of BzOEt is very nearly const. and appears to have a mean value of 1.1. It would seem, then, that the chem. character of the esters does not influence the general type of the curve showing the relation between the velocity const. and the compn. of the solvent medium. The curves may be divided into 4 phases, the relation between the value of k and the compn. of the solvent being linear for each phase. The critical points were found to be 80.5, 60 and 31% alc. These correspond very closely with simple integral ratios and it seems possible that complexes might exist composed of the 2 components of the solvent in the proportion of these %. Thus, 80.5% corresponds very closely to the complex $5EtOH.3H_2O$; 60% to $3EtOH.5H_2O$; and 30% to $EtOH.6H_2O$. The study is being extended. C. J. West

Classroom experiments demonstrating reaction velocity. E. Mannheimer. *Z. physik. chem. Unterricht* **34,** 118–123(1921).—A simple arrangement (suction flask and buret) is used to measure the rate of production of H_2 by small rods of Mg-metal from various acids of different concns. The time required to liberate some definite quantity of the gas is noted. "Strength" of acid or relative H-ion concn. of acids can be measured by this method; the effect of catalyzers (Cu or Zn salts) as well as the retarding effect of Mg salts, the anion of which is the same as that of the acid employed (law of mass action), can also easily be demonstrated. S. Morgulis

Reactions between ferrous oxide and carbon and between carbon monoxide and iron. IV. V. Falcke. Univ. Leipzig. *Z. Elektrochem.* **27,** 268–78(1921); cf. *C. A.* **10,** 3041.—Previous investigations on the equil. of the reactions between FeO and C and between CO and Fe are discussed briefly. It has been found exptly. that at temps. under 700° the equil. const., $\zeta = \frac{p^2CO}{pCO_2.RT.760}$, of the reaction $C + CO_2 \rightleftharpoons 2CO$, does not coincide with that obtained from measurements of the equil. of the reaction between FeO and C and between CO and Fe. From both this and analytical data it would appear that in this equil. the C does not play a role as a definite phase. The most probable explanation of this phenomenon is the previously accepted surmise that the equil. is detd. by the formation of carbide. H. Jermain Creighton

Interaction of oxalic acid with iodic acid. II. Influence of different catalysts. Georges Lemoine. *Compt. rend.* **173,** 7–13(1921); cf. *C. A.* **15,** 975.—The effect of temp., of amt. of catalyst, of size of particles, and of nature of gas adsorbed at low temps. on catalysts for the reaction of $(CO_2H)_2$ on HIO_3 was detd. by measuring the gas evolved. Spongy Pt, Pt black, wood charcoal and carbon from sugar were used. The particles except those of the Pt black were 1–2 mm. in diam. The grains of Pt black were about 0.1 mm. in diam. While the speeds of the reactions were more rapid

at higher temps. either in the absence or in the presence of the catalyst, the presence of the catalyst increased the rate of reaction by a higher factor at low temps. than at high temps. The rate of reaction increased with increasing wt., or fineness of division of the catalyst but was not proportional to either. The nature of the gas adsorbed had no effect on the catalyst as a catalyst. The two forms of C and the spongy Pt are called physical catalysts, but the effect of Pt black was so much greater than that of the others that its effect was considered chemical. F. E. BROWN

The catalytic action of salts of some metals in the reactions of organic compounds. ANTOINE KORCZYNSKI. *Bull. soc. chim.* 29, 283–90(1921).—When it is said that the catalytic action of an element is a function of its at. wt., it is generally supposed that the meaning is that elements in the same column of the periodic table will be found to act in a similar manner. Previously, however, it has been noticed that Fe, with approx. twice the at. wt. of Al, can replace the latter in the Friedel and Crafts reaction. The Sandmeyer reaction is produced not only by salts of Cu but also by salts of metals whose at. wts. are near that of Cu such as Cr, Mn, Fe, Co, Ni, and Zn. The first two and the last one of these do not show much action. Mo and Sn have no effect; but W with about three times the at. wt. of the active elements mentioned above, and U with four times that wt. are again active. In this case the "chemical resonance" or repetition of catalytic effects, seems to depend on approx. equal increments in at. wt. The at. wts. are not exact multiples, but there is identity of catalytic energy. Either W or WCl_6 is a catalyst for the bromination of benzene. An excess of bromine is not necessary. The product is a dibromobenzene even with an excess of Br. If $FeCl_3$ is used as a catalyst and the Br is present in excess C_6Br_6 is formed. The following elements or their chlorides or bromides catalyze the halogenation of aromatic hydrocarbons: Au, Al, Ga, W, Tl, Zr, Sn, Sb, Bi, Te, I, Fe, Mn, Mo, U, Th. If these are arranged in the order of at. wts. and the sum of the wts. of neighboring elements of lighter at. wts. be taken, often that sum will be the wt. of the atom of an element which is also a catalyst for this reaction. F. E. BROWN

Variation of the catalytic power of electrolytic platinum sols. A. DE GREGORIO ROCASOLANO. *Compt. rend.* 173, 41–3(1921).—The catalytic effects of colloids change much in short periods of time owing to ordinary changes in these systems. Electrolytic Pt sols were prepd. Some samples were stabilized with gelatin and some were not. Equal amts. of a sample of a catalyst were put in equal vols. of H_2O_2 and treated similarly in all particulars except that each successive expt. was started 1 hr. later than the preceding. The catalytic effect observed in the successive expts. with one sample of catalyst varied in amt. but the variation is not orderly. In all cases the catalytic effect of non-stabilized colloids was greater than for stabilized. Since increase of elec. charge on a colloid increases stability, the elec. charge cannot be the seat of the catalytic power. [Note by abstractor. The author seems not to have considered the possibility that a protective layer of gelatin on the catalyst might interfere with catalytic action.] F. E. BROWN

Double catalysis of vanadic acid and hydrogen peroxide. V. AUGER. *Compt. rend.* 172, 1355–7(1921); cf. *C. A.* 6, 1108.—Cain and Hostetter have expressed the opinion that the mutual reduction of vanadic acid and H_2O_2 in H_2SO_4 soln. is due to the catalytic effect of Caro's acid, which is formed in the mixt. Auger used colloidal suspensions of vanadic acid in solns. made acid with different concns. of each of HCl, H_2SO_4 and HNO_3. In all of these suspensions the addition of H_2O_2 resulted in a more or less complete reduction of the vanadic acid. In all of these cases it is possible that a peracid could be formed and act as a catalyst. $HClO_4$ and H_2O_2 do completely reduce vanadic acid. A water suspension of colloidal vanadic acid is reduced to the extent of about 2% by H_2O_2. Caro's acid poured in vanadic acid causes reduction of the latter

which is more complete as the concn. of the acid increases. The expts. show a parallelism between pervanadic and perchromic acid. There is a difference, however, in that the salts of V are oxidized by H_2O_2 and those of Cr are not. F. E. BROWN

Catalytic dehydrogenation of alcohols. E. K. RIDEAL. *Proc. Roy. Soc.* (London), 99A, 153–62(1921).—Though the dehydrogenation of EtOH and iso-PrOH is commercially important, physical and chemical data regarding their sp. heats, heats of combustion, etc., are not concordant. Substituting averages for the data required in the Nernst's approximation formula R. calcd. that the variation of the dissociation of these alcohols is large with a comparatively small change of temp. This agrees with Sabatier's exptl. results. R. detd. exptly. the dissociation const. for these alcs. for the temps. between 105° and 275°. The detns. were made with a const.-vol. thermometer with Cu as a catalyst. The pressure on the cooling curve was above that on the heating curve for all temps., showing some irreversible increase in pressure. The values were not widely different when low partial pressures were used. When ΔU_0's are calcd. from R.'s data the agreements with the exptl. data are good. Tables of data and equations for calcn. of results are given. F. E. BROWN

The mechanism of catalysis. CAMILLE MATIGNON. *Chimie & industrie* 6, 7–10(1921).—Summary of C.'s conceptions of the mechanism of catalysis (reprinted from a review of his scientific works, published in 1907). Reactions which are thermodynamically possible, *i. e.*, in which the uncompensated heat is positive, do not occur below a certain temp. Between the temp. at which such a reaction occurs at an appreciable rate and that below which it does not occur at all there is a range where it occurs with extreme slowness. The function of the catalyst is to replace this reaction by 2 or more other reactions which occur readily in the temp.-range above-mentioned, and which give the same final result as the first reaction. Various deductions are made, many of which have since been proved experimentally. A. P.-C.

Exchange of ions on the surface of minerals. G. TAMMANN. *Z. anorg. allgem. Chem.* 113, 149–62(1920).—T. has measured the potential of galena, litharge, Zn blende graphite, magnetite, Fe pyrite, Mn silicide, and orthoclase against the normal H electrode, $Zn|2N\text{-}ZnSO_4$ soln., $Pb|PbCl_2(satd.)|,Cu|CuSO_4|$, and $Ag|Ag_2SO_4(satd.)$, under various conditions of polarization, and from the results has shown that minerals, such as sulfites and silicates, suspended in aq. solns., exchange their less noble cations for the more noble H cation. This H charge then protects them from exchange with metal ions, which are less noble than the H ion. In the case of the sulfides, the exchange takes place rapidly, but with silicates extremely slowly. The present results confirm the work of Rubens (*Sitzb. kgl. Akad. Wiss. Berlin.* 1, 47(1917)), who found that binary salt crystals reflected and absorbed certain ultra-red rays very strongly, and in order that this could occur, it is necessary that the points of crystal lattice must be occupied by ions, a demand which the present work substantiates. The present work also explains the *adsorption of* very small quantities of *radioactive substances* and the presence of small quantities of *noble metals in the compds. of less noble metals.* J. C. S.

The influence of the solvent upon ionization and the accompanying heat effect. SIDNEY M. NEALE. *Trans. Faraday Soc.* (adv. copy) 1921, 4 pp.—The degree of ionization of any substance in soln. depends largely on the solvent, and one would expect a variation of the heat of ionization with different solvents. This would indicate that the internal energies of the mol. species vary with the solvent as well as with the temp. Conductivities of solns. of picric acid in varying mixts. of H_2O and acetone were measured at 25° and 35° and the value of Ostwald's const. K was calcd., and then that of the heat of ionization from the equation $d\ln K/dT = \text{heat absorbed}/RT^2$. In passing from pure water to 93.8% acetone K falls from 0.2 to 0.002 but still deviations

from Ostwald's diln. law manifest themselves. In anhydrous acetone K is of the order of 10^{-9} and the diln. law holds strictly. Thus the anomaly of strong electrolytes, it seems, should be referred to the mutual effect of the system solute plus solvent rather than to high degree of ionization. The heat of ionization varies with the solvent, passing through a minimum at 70% acetone. The equiv. conductivity is a minimum at the same point. In the case of *p*-nitrobenzoic acid the heat effect is sensibly zero both in water and in 44.35% acetone though in the latter case K has fallen 5% of its value in water. A. E. STEARN

Note on the abnormality of strong electrolytes. DAVID LEONARD CHAPMAN AND HERBERT JOHN GEORGE. Jesus College, Oxford. *Phil. Mag.* **41**, 799–801(1921).—A criticism of a theory of electrolytic dissociation of Ghosh (*C. A.* **12**, 1609, 2268; **13**, 88, 205) based on the assumption of complete dissociation of the electrolytes. Only the fourth postulate, that the free (conducting) ions are those whose kinetic energy is greater than the work to be done in sepg. them to infinite distance, is discussed in the present paper. According to Ghosh it follows that the kinetic energy of a free ion must exceed $A/2$, half the work to sep. the ion from its partner, the number of ions satisfying the condition being according to Ghosh $Ne^{-A/2kt}$, in which N is the total number of ions, k the gas const. for a single mol., and t the abs. temp. From the kinetic gas theory C. and G. develop a different expression. A comparison is made for different dilns. of the ratio μ_v/μ_∞. The values calcd. from the expression of C. and G. show a good agreement with observed values of dissociation, while those of Ghosh show a discrepancy which becomes large at the higher concns. The discussion is carried out for the simplest case, a uni-univalent salt, KCl. S. C. LIND

The dielectric constants of electrolytic solutions. R. T. LATTEY. Elec. Lab., Oxford. *Phil. Mag.* **41**, 829–48(1921).—The methods in use for detg. the dielec. const. of H_2O and solns. are critically reviewed. A complete bibliography is collected. A method is described for making the necessary corrections for cond. Expts. were carried out with an improved form of app. which is shown diagrammatically. The mean obtained for the dielec. const. of H_2O at 18° from a large number of detns. is 81.05. Coolidge's temp. coeff. was employed to reduce all the observations to a common temp. The mean for glycerol is 51.15. The dielec. consts. were detd. for a few aq. solns. For a sugar soln. contg. 6.84% sugar the value was 81.2, for 11.92%, 69.8. Values were also obtained for KCl solns. of several concns. For $N = 0.00755$, dielec. const. (D. C.) = 80.25; for $N = 0.00755$, D. C. = 66.25. For $CuSO_4$ of $N = 0.00114$, D. C. = 75.2; for $N = 0.00228$, D. C. = 78.2, and for $N = 0.00456$, D. C. = 73.9. The D. C. of water was found to be independent of the frequency from wave lengths of 17 to 52 meters. S. C. LIND

The conduction of electricity in gases. G. HOLST AND E. OOSTERHUIS. *Physica* **1**, 78–87(1921).—The first part of the paper deals with expts. with tubes contg. a hot cathode. In A at moderate pressures (1 cm.) and low current densities resonance occurs, but no trace of ionization was found. Under similar conditions Ne shows a very pronounced ionization, the gas becoming luminous. This luminosity makes it possible to study the phenomena in Ne by visual observation. In further expts. with Ne-filled tubes contg. the hot filament mounted axially in a cylindrical anode, at 20 v. a luminous layer is observed in the anode. This layer moves toward the cathode when the voltage is increased, and at 40 v. a second layer appears, and at 60 v. a third layer. A similar effect may be produced by raising the filament temp. at const. anode potential. The second part of the paper deals with expts. on Ne-filled tubes with cold electrodes. The sparking potential was found to depend on the nature of the cathode material. If, as has been supposed, the positive ions liberate fresh electrons from the cathode, metals which easily emit electrons should show low values of the sparking

potential. The expts. showed that this is true. With very small currents between parallel electrodes a striated discharge was observed, which clearly shows that the electrons are liberated from the cathode and that recombination is an important factor in preventing the current from reaching a high value. L. H. ADAMS

The laws of moduli and the theory of electrolytic dissociation. Experimental determination of the modulus of refraction. VICTOR J. BERNAOLA. *Anales soc. quim. Argentina* **8**, 17–31, 73–99(1920).—The article deals with the calcn. of the sp. gr. and *n* of a dil. soln. of any common salt. It cannot well be abstracted. Many tables of consts. and a bibliography are included. L. E. GILSON

The thermoelectric power of nickel-iron alloys. A. PEPE. *Rend. accad. sci. Napoli* **27**, 60–6(1921).—Measurements were made of the e. m. f. of couples of pure Fe or pure Cu against alloys of Fe and Ni contg. 49, 44, 36 and 22% of Ni, and pure Ni, at temps. from −185.2° to 843.4°, the temps. being detd. by a Le Chatelier Pt–Pt-Ir couple. The tables give the e. m. f. in millivolts.

Couple.	Temp.					
	−185.2°	21.18°	99.83°	205.57°	303.2°	412.8°
Fe–51% Fe, 49% Ni	— 9.989	1.0883	4.952	9.071	11.557	13.0683
Fe–56% Fe, 44% Ni	— 9.648	1.0145	4.435	7.735	9.337	9.9517
Fe–64% Fe, 36% Ni	— 5.4705	0.5073	2.0539	3.285	3.7117	3.795
Fe–78% Fe, 22% Ni	— 3.3528	0.3797	1.6992	3.1057	3.9363	4.1997
Fe–Ni	— 4.876	0.6360	3.0643	6.195	8.588	10.5658

Couple.	Temp.				
	499.08°	592.49°	685.7°	758.3°	843.4°
Fe–51% Fe, 49% Ni	13.0733	12.748	12.3335	12.02081	1.778
Fe–56% Fe, 44% Ni	9.673	9.297	8.9277	8.677	8.4347
Fe–64% Fe, 36% Ni	3.4981	3.1212	2.8206	2.7131	2.5962
Fe–78% Fe, 22% Ni	4.2882	4.3163	4.3751	4.4402	4.6058
Fe–Ni	11.7060	13.163	15.048	17.2344	19.035

Couple.	Temp.					
	170.5°	246.46°	309.02°	413.64°	502.27°	591.15°
Cu–51% Fe, 49% Ni	6.678	9.0606	10.5967	12.4739	13.232	13.7553
Cu–56% Fe, 44% Ni	5.6365	7.3535	8.3054	9.3564	9.8358	10.2677
Cu–64% Fe, 36% Ni	1.997	2.3913	2.6815	3.2084	3.6603	4.0943
Cu–78% Fe, 22% Ni	1.3625	2.094	2.614	3.6195	4.4841	5.2769
Cu–Fe	−1.1151	−1.2281	−1.1256	−0.5659	+0.1824	0.9445
Cu-Ni	4.1055	6.0945	7.6294	9.9777	11.9602	14.184

Couple.	Temp.				
	687.44°	744.28°	787.2°	848.43°	900.2°
Cu–51% Fe, 49% Ni	14.153	14.420	14.563	14.724	14.861
Cu–56% Fe, 44% Ni	10.7325	11.018	11.1978	11.362	11.5
Cu–64% Fe, 36% Ni	4.6044	4.9178	5.1721	5.4742	5.768
Cu–78% Fe, 22% Ni	6.1521	6.6003	7.0231	7.567	8.013
Cu-Fe	1.7345	2.1341	2.4221	2.8787	3.185
Cu-Ni	16.6224	18.408	19.7044	22.10	24.671

M. R. SCHMIDT

Copper standard cell. J. OBATA. *Proc. Phys. Math. Soc. Japan* **2**, 223–9(1920).—See *C. A.* **14**, 2744. F. P. PHELPS

Weston cell containing acid electrolyte. J. OBATA. *Proc. Phys. Math. Soc. Japan* **2**,

232–6(1920); *Science Abstracts* **24A**, 223.—F. E. Smith has shown that the Weston cell is more const. if the electrolyte is made acid. O. has prepd. several cells containing electrolyte acidified to various strengths and studied their properties. The e. m. f. decreases linearly as the acidity increases; the acidity e. m. f. relation is $\Delta e = 85.5\ x$, where Δe is the decrease in voltage expressed in 10^{-5} volt, and x the acidity of the electrolyte expressed in terms of normal acidity. Smith observed that when the soln. of $CdSO_4$ is made up from normal acid satd. with $CdSO_4$ the e. m. f. is diminished by 0.00065 v. O.'s results are in exact agreement. After the acid cells have attained their normal value they are found to be extremely const. The temp. coeff. of a cell contg. 0.76 *N* acid is greater than that of the non-acid cell by 11%. F. P. PHELPS

The absolute measurement of resistance. I. Historical account of the absolute determination of the unit of electrical resistance. RICHARD GLAZEBROOK. *Proc. Phys. Soc.* (London) **33**, 126–31(1921).—G. gives a historical outline of important events in the establishment of the ohm as the practical unit of elec. resistance, and of the standards which represent it. **II. Two proposals: (a) Respecting the present system of electrical units; and (b) on a lecture demonstration of the absolute determination of resistance.** F. E. SMITH. *Ibid* 131–4.—Since at the present time an accuracy of ±2 parts in 100,000 in the abs. measurement of resistance is attainable (a degree of accuracy equal to that attainable in the reproduction of the international ohm) it is proposed that elec. resistances be expressed in ohms (10^9 C.G.S. units) without qualification, such as legal, international, etc., other elec. quantities as the ampere and volt to be expressed similarly. An advantage of this change would be that physical quantities measured electrically would have the same value as when measured by other methods instead of a difference of several parts in 10,000 as results when the elec. quantities are expressed in international units. The second proposal is, that teachers should seriously consider introducing an expt. in the abs. measurement of resistance to illustrate their lectures, in order to make the students more familiar with abs. measurements and consequently more interested in them. An app. similar to the original British Assoc. coil is described and the theory of its operation given. C. C. VAN VOORHIS

A general law of thermodynamics. W. KASPEROWICZ. *Electrochem. Z.* **27**, I, 71(1921).—A brief note on Nernst's law discussing the possibility of detg. the value of the max. temp. of a system. W. E. RUDER

The heat of formation of beryllium oxide and beryllium chloride. W. MIELENZ AND H. VON WARTENBERG. *Z. anorg. allgem. Chem.* **116**, 267–8(1921).—Be was prepd. according to the method of Lebeau, by electrolyzing the double salts of BeF_2 and NaF; the metal thus prepd. still contained 30.55% BeO as only impurity. The heat of formation was measured by directly combining the metal with O_2 and Cl_2 in a calorimeter, $Be + Cl_2 = BeCl_2 + 112.6 \pm 0.4\%$ Cal. $Be + O = BeO + 135.9 \pm 0.9\%$ Cal. E. FIERTZ

Specific heats of technical copper-zinc alloys at higher temperatures. FR. DOERINCKEL AND MAX WERNER. Eberswalde Brassworks. *Z. anorg. allgem. Chem.* **115**, 1–48(1921).—Rather careful estimates of the precision indicate a max. error of 1.5% and the agreement is nearly always better than that. A *furnace* consisting of a *Cu* tube 2-mm. thick, covered with chamotte and water glass, and wound with nichrome wire, lasted for over 50 expts. at 800°. A *neutral atmosphere* was obtained within it by flooding with CO_2. Although this gas dissociates at the high temps. used, oxidation by it was inappreciable. Temp. fluctuations due to the gas stream gave trouble till the gas was run in through lumps of chamotte which filled the upper part of the furnace Samples which had not been brought to equil. showed an abnormally high sp. heat between 400° and 500°, which was found to be uncertain and was not definitely accounted for by various expts. The suggestion is made that it may be due to some sort of an

inversion which is much affected by variation in the compn. of the impurity present in com. brass. The results from "tempered" brass, *i. e.*, brass annealed at very high temps., are expressed in the form $c_m = a + b(T_2 - t_2)$, where c_m is mean sp. heat and T_2 and t_2 upper and lower limits of the temp. interval, resp. This formula makes the sp. heat over a very small interval equal to a, and therefore const. at all temps., which is absurd, but apparently is valid (or nearly so) for $t_2 = 18°$, for which it was derived from the data. The values found for a and b are:

Concn. % of Cu.	*a.*	*b.*
84.8	0.0922	0.0000130
71.0	0.0916	0.0000155
66.4	0.0909	0.0000166
63.0	0.0902	0.0000228
57.3	0.0895	0.0000335

For compns. where β-brass is the prevailing phase, 53% to 65.8 Cu, a increases, and b decreases, with Cu content. In the region of the α crystals above 65.8 Cu the same changes continue, but less rapidly. Hence the sp. heat of any brass varies linearly with temp. within the limits of precision attained; at high temp. the sp. heat decreases sharply with Cu content in the β region (from 0.121 to 0.104 at 800°), more slowly in the α region; below 100° there are increases; at about 100° the sp. heat varies little with compn. W. P. WHITE

Thermal expansion of some substances. I. KARL SCHEEL. Phys. Tech. Reich. *Z. Physik* **5**, 167–72(1921).—The measurements are made by a direct method for large specimens and by a Fizeau dilatometer for small ones. Values are given from −190, to +500° for Al, Mg, Ag, quartz, porcelain and some Jena glasses, and from −190 to +100° for invar and some other special alloys. II. J. DISCH. Phys. Tech. Reich. *Ibid* 173–5.—D. measures with a Fizeau dilatometer the values for Cr, Mn, Mo, Ni Ta, W, and "Elektron." F. C. HOYT

Temperature correction in bomb calorimetry. N. H. ENGSTRÖM. *Tek. Tid. Kemi o. Berg.* **51**, 18–21(1921).—A formula is evolved for the correction of temp. in bomb calorimetry. This formula is for general use where the tedious calcns. by the application of the classic equation of Regnault-Pfaundler is not absolutely necessary. It is given as follows: $k = (1 - n)v - {}_1v$. The order and significance of the letters are the same as in the Reg.-Pf. equation. This new formula was tested by a large number of detns. and its error falls within the limits ± 0.001–0.003°. The error was seldom as high as ±0.003°. A. R. ROSE

The variation of the diamagnetic constant of water with the temperature. BLAS CABRERA. Univ. Madrid. *Anales soc. quim. Argentina* **8**, 283–92(1920).—A detailed illustrated account of the detns. made. The article cannot well be abstracted. L. E. G.

Magnetic susceptibility of certain natural and artificial oxides. E. F. HERROUN AND E. WILSON. *Proc. Phys. Soc.* (London) **33**, 196–206(1921).—The susceptibility of Fe_2O_3, as occurring in nature, varies through a wide range, but in the case of artificial prepns. the range of variation seems to be much greater. The highest susceptibility exhibited by Fe_2O_3 occurs when either FeO or Fe_3O_4 is oxidized at a high temp. in the anhydrous condition. From hydrated Fe_3O_4 the susceptibility, though considerable, is much less. The lowest susceptibility is obtained from native hematites or naturally oxidized chalybite, or by the ignition or pptn. of ferric salts. It appears that the passage through the stage of Fe_3O_4 impresses more pronounced magnetic properties upon the resulting Fe_2O_3. The susceptibilities of a number of ferrites were measured, of which that of Cu ferrite is most conspicuous, its susceptibility being higher than those of Co or Ni ferrites or any similarly constituted compd. except Fe_3O_4 itself. Heating feebly mag-

netic Fe_2O_3 with a basic oxide, as CaO or MgO, increases susceptibility (confirming List and others). When higher susceptibility has been produced by heating Fe_2O_3 with a basic oxide such as Ag_2O or HgO, subsequent removal of the metal leaves the Fe_2O_3 in a magnetic condition. The chem. compds. formed when Fe_2O_3 is replaced by Al_2O_3 show no definite increase in susceptibility which is in marked contrast with the ferrites. In the cases of Co and Mn the susceptibilities of the different oxides show a steady decrease with increase of O, and unlike Fe, there is no increase in the susceptibility of Co_3O_4 and Mn_3O_4 corresponding with Fe_3O_4. Though the susceptibility of Cu is negative, that of each of its oxides is positive but small in magnitude. C. C. V. V.

Observations on abnormal iodine values, with special reference to the sterols and resins. I. S. MACLEAN AND E. M. THOMAS. *Biochem. J.* **15**, 319–333(1921).—The Hübl values of the sterols are variable but indicate approx. the number of double bonds believed to be present in the mol. The Wijs numbers are much greater and probably indicate that substitution has also taken place. In the sterols and resins the presence of a condensed ring nucleus contg. one or two double bonds influences the amt. of substitution produced by the Wijs reagent. The actual number of double bonds present is approx. indicated if the I value is detd. by Hübl's soln. In any fat contg. appreciable quantities of sterol, the Hübl I value more accurately represents the degree of unsatn. of the mixt. than does the Wijs value. The I values of phenol, α-naphthol, fatty carbonyl compds. and phenanthrene hydrocarbons were also examd. B. H.

Methods for the production and measurement of high vacua. SAUL DUSHMAN. *Gen. Elec. Review* **24**, 669–80(1921); 7 illus.; cf. *C. A.* **13**, 2369.—The present instalment deals with the elec. cleanup of gases at low pressures, more especially with effects observed in hot cathode devices and incandescent lamps. The theory of phosphorus cleanup in lamps is also discussed. The researches of N. R. Campbell and J. W. H. Ryde (*C. A.* **15**, 466) are reviewed at length. C. G. F.

Normal pressures. E. BRAUER. *Z. angew. Chem.* **33**, Aufsatzteil, 80(1920).—B. urges the importance of adopting standard pressures, especially for such work under vacuum as the detn. of b. ps., etc., and recommends the use of the bar as the unit of pressure. One atm. = 1013200 bars, so that 10 kilobars = 7.5 mm., and 1000 kilobars = 750 mm. Hg. A cut shows an app. suitable for obtaining reduced pressures. A regulating cock is inserted in the vacuum line and the fine adjustments are made by means of 2 tees, 1 inserted between the boiling flask and a manometer and the other between the receiver and the regulating cock. The stem of each tee has a cock, and outside of the cock the stem is drawn to a capillary tube to admit small quantities of air. J. H. M.

Methods of measuring the opacity of liquids (HOLKER) **11B.** Relation between the microscopic appearance of precipitated calcium oxalate and the opacity of its suspensions (HOLKER) **11A.**

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Official Year Book of the Scientific and Learned Societies of Great Britain and Ireland. London: Charles Griffin and Co., Ltd. 351 pp. 15s. For review see *Analyst* **66,** 261(1921).

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

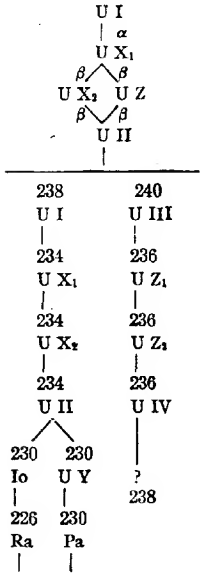
GERALD L. WENDT

Future developments of theoretical chemistry. IRVING LANGMUIR. *Chem. Met. Eng.* **24,** 553–7(1921).—A review of the advances in theoretical chemistry in the past and a discussion of the effect of knowledge of atomic structure on the science of chemistry and future chemical education. "Knowledge of atomic structure promises to make chemistry a deductive science and a science fundamentally simple compared to what it is now." N. D. CHERONIS

Discovery of radium and its scientific consequences. HERBERT N. MCCOY. *Chem. Bull.* (Chicago) **8,** 149–51.—A review. R. S. LANDAUER

Quantum theory: The photo-electric effect of subdivided light quanta. C. RAMSAUER. *Ann. Physik* **64,** 750–8(1921).—The author attempts to put to an exptl. test, by means of the photo-elec. effect, the well known hypothesis that it is the existence of energy in definite quanta in the form of trains of light waves which gives rise to quantum emission of photoelectrons. If it is assumed that (1) single light quanta are coherent wave trains of small cross-section, (2) the behavior of these single quanta must be such that the whole light beam follows optical laws, and (3) the photoelec. effect consists of the conversion of a light quantum into the equiv. electronic energy through the agency of the atoms, then if a beam of light be polarized by passing through *two doubly refracting crystals* set at an angle A between their principal planes, *any light quanta which get through must be subdivisions of the whole original quanta.* Since this is the case the energy of the electrons emitted by such light quanta must be changed, for their energy comes from the values of the quanta of energy in the wave train. Thus the electrons liberated by light which had passed through two polarizing crystals when compared to those liberated by the original light should suffer: (1) a complete change in their energy distribution, (2) a change in the number of electrons emitted with a change in the angle A, which differs markedly from the variation of that number according to $\mathrm{Cos}^2 A$, which is to be expected if there is no division of the wave trains into quanta. These conclusions are tested experimentally on photo-electrons. R. finds no change in the energy distribution curves even in the case where the quanta would have

been, on the basis of his reasoning, cut down to $^1/_4$ of the initial quanta. He further found that the numbers of electrons liberated followed the $\cos^2 A$ law very closely. He concludes that the quantum-like behavior of photo-electric processes must then be the result of the mechanical processes of absorption of the light energy taking place in the atom. The behavior is certainly not caused by single light quanta being present in the wave trains of the light as definite entities. L. B. LOEB



A new radioactive substance in uranium. OTTO HAHN. *Ber.* **54B**, 1131–42(1921).—In a further search for the relation between the Act series and the U series a new radioactive substance has been found. It is sepd. with protoactinium (Pa) and is isotopic with it. Until its origin is clear it will be called U Z. It has a half life of 6.7 hours and gives off β-rays of great complexity which are half absorbed by layers of Al from 0.014 to 0.12 mm. thick. It is present in only very small quantities and its ray intensity is about 0.25% of that of U X ($U X_1 + U X_2$) which comes from the same quantity of U. Two possibilities are suggested for the origin of U Z: (1) (Represented by diagram above the horizontalline.) This is not very probable as such a double decompn. has never been observed in a radioactive change.

(2) (Represented by diagram below the horizontal line.) There may be a new radioactive series isotopic with the ordinary U series. In this scheme there would be $U Z_1$ and $U Z_2$ by analogy to $U X_1$ and $U X_2$. It is very improbable that U I represents the mother substance of U Z and that U Z results from U I by the emission of an X_2 particle of mass 3. It is more probable that there is a new U III, isotopic with U I, of mass 240. There is no definite evidence for either of these assumptions so the question remains unanswered.

MARIE FARNSWORTH

Mass spectra and atomic weights. FRANCIS W. ASTON. *J. Chem. Soc.* **119**, 677–87(1921).—A lecture delivered before the Chemical Society (London). See *C. A.* **14**, 3578; **15**, 335. N. D. CHERONIS

Color and chemical constitution—with regard to the subatomic structure and the nature of the electron bond. GILBERT N. LEWIS. *Chem. Met Eng.* **24**, 871–5(1921).—In the mols. there are 2 sets of charged particles capable of acting as oscillators, the positively charged nuclei and the electron. On account of the relatively high mass of the positive particles it seems probable that they never, or almost never, are capable of vibrating with a frequency sufficiently high to come within the scope of the visible spectrum, but rather cause absorption in the ultra-red. On the other hand those light and indeed almost massless particles called electrons are usually held lightly enough so that their natural period is well above that of the visible spectrum and they can therefore absorb the ultra-violet region. Thus in the great majority of chem. compds. which are colorless the positive parts have too low a frequency and the negative parts too high a frequency to affect the visible spectrum. If, however, the constraints under which the electrons are held are in some way loosened, their frequency of vibration will diminish, and then ultimately they may become so loosely held as to absorb in the visible. A number of diagrams showing the structure of atoms, the electron bond, the double bond and the tendency to conform to certain very simple types are given. N. D. C

Positive and negative photoelectrical properties of molybdenite and several other substances. W. W. COBLENTZ. Bur. Standards, *Sci. Paper* **398**, 596–639(1920); cf. *C. A.* **13**, 1417; **14**, 149, 1260.—This paper sums up some of the previous work on photoelectrically sensitive substances and reports new data on molybdenite, silver sulfide, and stibnite. A large quartz prism and 500-watt gas-filled tungsten lamp gave intensities of light so great that observations were possible throughout the visible spectrum and well into the ultraviolet. For a sample of Japanese stibnite, the resistance in the dark decreased with increase of voltage and with time at constant voltage. Maximum change of cond. on exposure to light was reached in 5–30 sec. at room temp. At lower temps. longer times were required. Thin samples reached equil. in less time than thicker ones. As the temp. decreased the maximum change of cond. was caused by shorter wave lengths. The conduction of stibnite was found to be unipolar. One sample gave a galvanometer deflection of 65 cm. when the current flowed in one direction and only about 16 cm. when no change, except the reversal of the direction of current flow through the crystal, was made. But this change in cond. had no effect on the spectrophotopositive reaction of the sample. Acanthite, Ag_2S, was found to be photopositive. At 0° the maximum effect was followed by a decrease, even in the light, and when the light was shut off the cond. fell below the ordinary cond. in the dark but soon recovered its normal dark cond. Light waves 0.3 μ in length were most effective. The resistance was affected by the direction of the current but the photoelec. reaction was not. At lower temps. the drop below the ordinary dark cond. disappeared except for momentary reactions. There were some momentary increases of resistance on exposure and some momentary decreases of resistance after the light was shut off. The molybdenite had not only different cond. for different directions through the crystal but the direction of greatest cond. depended on the temp. The reversal occurred at about +5°. One small area was found which was many times as sensitive to light as the remainder of the crystal of molybdenite. With wave length 0.5876 μ and temp. −101°, 12 volts gave only a decrease of resistance, while 33 volts gave only an increase of resistance. For wave lengths greater than 0.67 μ all voltages gave a photopositive reaction. Intermediate voltages produced a cycle of changes which showed a decrease of cond. at one stage and increase at another. Change of amt. of resistance in the circuit had the same effect as change of voltage. The photonegative property of this crystal seems to be due to the magnitude of the current flowing through it. At moderate rately low temps. (−10° to −25°) unsteadiness of current flow developed during recovery from an exposure. The spectrophotoelec. sensitivity of molybdenite also varied sharply with the length of the light wave used. The reaction changed from increased resistance to increased cond. with a change of 0.001 μ in wave length. The photopositive tendency and the photonegative tendency are two contending forces, acting simultaneously. The photonegative action builds up slowly and is predominant on high voltages; the photopositive action builds up rapidly and predominates on low voltages. Stratton believes that molybdenite and stibnite are superior to selenium as a material for *radiophonic signalling devices*. A drawing and discussion of such a device is given.

F. E. BROWN

A quantitative determination of the number of electrons liberated by canal rays. H. BAERWALD. *Ann. Physik* **65**, 167–87(1921).—The number of secondary electrons emitted per unit charge carried per second by the positive primary rays was first detd. Then the primary beam was analyzed by deflection in an elec. field, and the ratio of the numbers of positive, negative, and uncharged particles present in the beam was detd. with a bolometer. The results in gases were mostly obtained in H_2. In metals they were obtained for *brass*. For gases the author found an increase in the number of secondary rays per cm. path which was proportional to the pressure. He also found an in-

crease of this same quantity proportional to the potential acting on the primary rays. The number of secondary electrons formed per cm. path of the rays in H_2, if computed back to atm. pressure, fits in well with the ionization-velocity curve found for α-particles, provided the max. of the α-particle curve is displaced to coincide with the optimum value of the velocity for ionization by electrons at 6.8×10^9 cm./sec. In the region of velocity of the positive rays from 0 to 2.5×10^8 cm./sec. there is no evidence of a change in the nature of the impacts of these rays with the gas mols. from impacts ending in reflection to impacts ending in an interpenetration of the rays with the mols. This change should take place at about 2×10^8 cm./sec. The concn. of electrons in the gas space was found to be small. At 1 mm. there was one electron to 200 mols. This small concn. of electrons, as well as the fact that there are 4 times as many uncharged carriers present in the beam as there are positively charged ones, demands a theory of the change in charge of the positive rays which depends for the neutralization of the charges of the rays rather on the removal of an electron from a neutral mol. than on the neutralization of this charge by the picking up of an electron. With metals *in vacuo* the number of secondary rays increases with the velocity of the primary rays to a definite limit. This seems to be chiefly detd. by the thickness of the layer through which the electrons can escape. The limit is for H_2 canal rays striking brass about 5–6 electrons per primary particle. L. B. Loeb

Ionization of argon by slow electrons. Georges Déjardin. *Comptes rendus* **172**, 1347–50(1921).—A simple three-electrode tube is described. The critical potential of argon is found to be 15 ± 0.5 v. Corrections are made for the fall of p. d. along the wire, the speed of emission of electrons, and the difference of p. d. between the incandescent filament and the anode. A p. d. of 16.2 v. is necessary before any luminosity is visible. This is called the illumination potential. Spectra of the gas between the plate and filament were taken, and with p. d. of from 16.5 to 30 v., the red spectrum of A showed especially the lines between 4045 and 4272. When Hg vapor is put in the tube the strongest line (4358) corresponds to a potential of 10.5 v., which is the ionizing p. d. of Hg vapor. The most intense rays in the A spectrum were obtained at a p. d. of 15 to 16 v. R. S. Landauer

The molecular theory of refraction, reflection, dispersion, and extinction. W. Bothe. *Ann. Physik* **64**, 693–712(1921).—This paper is a mathematical discussion of refraction, reflection, dispersion, and extinction of light waves in homogeneous isotropic media, in terms of frequency and density of mols. and magnetic and elec. fields. B. concludes that there is no essential difference between dense and rare media. They differ only in degree. The density dets. the proportion of direct and of scattered rays, both of which are always present. The conclusions have a meaning even when applied to vacua. The failure theory furnishes 2 simple principles: one for refraction, reflection, dispersion, and absorption, the ordered part; and a second for the disordered part, dispersion; and an exact formula for the intensity of dispersed light and the extinction coeff. which is applicable to the whole spectrum. Resonance radiations and opalescence radiations are not truly different; nor are selective and non-selective absorption. The Keesom-Einstein radiations and Rayleigh-Planck radiations are identical. F. E. B.

Report on instruments and methods of radiometry. W. W. Coblentz. *J. Optical Soc. Am.* **5**, 259–68(1921).—A description of the important radiometric instruments, including the thermopile, bolometer, radiomicrometer and Nichols radiometer. A bibliography is given. R. S. Landauer

The Shimizu-Wilson cloud-condensation apparatus. Anon. *Electrician* **86**, 720(1921); *Engineering* **111**, 692(1921).—A modification of the original Wilson app. by the aid of which the continuous emission of α- and β-particles and of electrons,

liberated by X-rays, can be observed and photographed. The operation is made continuous by the use of a piston reciprocating at a rate adjustable between 50 and 200 periods per min. The field is vertical, and a film of gelatin, made conducting, on the inside of the glass plate of the condensation chamber serves as the neg. electrode. Illustrations of the app. are given. W. E. RUDER

Wave length of hard gamma rays. ARTHUR H. COMPTON. Wash. Univ. *Phil. Mag.* **41**, 770–8(1921).—A new method of measuring the wave-length of high frequency radiation is proposed, consisting in observing the diffraction pattern due to the individual atoms. After a discussion of the theory underlying the method, a description is given of the exptl. arrangement, which consists in the use of thick rings of Cu and Pb as the scattering media. Some uncertainty exists as to the proportion of radiation which is truly scattered and that which is fluorescent even at the smaller angles of incidence; the ratios of the observed intensity for Pb and for Cu are reported at angles of 30°, 20°, 15° and 10°, and the relative intensity per electron is calcd. after making the necessary corrections. The values for the three larger angles are around 0.85 to 0.89 for the ratio Pb/Cu, considerably below theoretical unity. At 10° the ratio rises to 0.95, and while there is considerable uncertainty involved, it is believed the rise is not accidental, and that the theory for small angles is supported. On this basis the wave length of hard γ-rays after traversing about 8 mm. of Pb is calcd. to be 0.025 to 0.030 Å. S. C. LIND

Scattering of X- and γ-rays. J. A. GRAY. McGill Univ. *J. Frank. Inst.* **190**, 633–55(1920).—When an ordinary beam (*i. e.*, a beam not obtained by reflection from crystals) of X- or γ-rays is scattered, the rays which are scattered in any definite direction are of quite a different type from that of the primary rays. The type of the scattered rays depends on that of the primary rays, the angle of scattering, and possibly the nature of the scattering material. As the angle of scattering increases, the scattered rays have less and less penetrating power than the primary rays. The distribution of the scattered radiation for all types of X- and γ-radiation is similar; less radiation is scattered through 90° than in any other direction. Exptl. results may be explained by the hypothesis that X-rays consist of a series of pulses. If the primary rays be rays of definite wave length, the scattered rays, produced by reflection from a crystal, should be of the same wave length. The effect of scattering in absorption expts. is discussed.

JOSEPH S. HEPBURN

Some problems in the biological action of radiations (RUSS) **11A.** Effect of electron emission on the temperature of the filament and anode of a thermionic valve (STEAD) **4.** The dielectric constants of electrolytic solutions (LATTEY) **2.** The critical energy increment and Trouton's rule (RIDEAL) **2.** Dimensional consideration on the basis of the law of equipartition (SCHILLER) **2.**

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CENTNERSZWER, M.: **Das Radium und die Radioaktivität.** Berlin und Leipzig: Verlag von B. G. Teubner. M 350 and Teuerungzuchlag. For review see *Z. öffentl. Chem.* **27**, 132(1921).

NEUBURGER, M. C.: **Neuere Ergebnisse der Forschung über d. Radio aktivität des Kaliums u. Rubidiums im Letzten Dezennium.** Stuttgart: Verlag v. Fredinand Enke. M 2.50.

4—ELECTROCHEMISTRY

COLIN G. FINK

Charles Edward Skinner. ANON. *Elec. World* **78**, 252(1921); 1 illus.—Biographical sketch. "The most important of his contributions to science and to the industry is undoubtedly his work on insulation." C. G. F.

Electrometallurgy and electrochemistry of the rarer metals in recent years. F. PETERS. *Glückauf* **57**, 54–8(1921).—A detailed review. C. G. F.

Applied electrochemistry during 1919. GIORGIO WEDARD. *Ann. chim. sci. ind.* **37**, 49–52(1921).—A short review. E. FIERTZ

Recent progress in electrometallurgy. R. LEVATEL. *Outillage* **209**, 598–600(1921). C. G. F.

Recent developments in electric smelting. ANON. *Industrie électrique* **30**, 208–10 (1921).—A review. C. G. F.

The production of ferro alloys in the electric furnace. KARL DORNHECKER. *Schweiz. Chem. Ztg.* **1920**, 605–11.—A review. C. G. F.

Modern electric furnaces for nonferrous metals and alloys. KARL DORNHECKER. *Schweiz. Chem. Ztg.* **1921**, 13–5, 39–44.—A review. C. G. F.

The development of the electrometallurgy of iron and steel within recent years. KARL DORNHECKER. *Schweiz. Chem. Ztg.* **1921**, 257–60; 3 illus.—A review. C. G. F.

Pig iron held in molten condition in Baily furnace. ANON. *Elec. Rev.* (Chicago) **79**, 169(1921); 1 illus.—The test conducted with a Baily furnace shows a remarkable lack of variation in the composition of the pig Fe remaining in the furnace in a molten condition for a period of 24 hrs. The furnace was of 105 kw. capacity provided with a clay hearth, standard resistor and tilting gear. The diam. of the furnace was 7 ft. and its capacity 1 ton. Borings which heretofore could not be handled readily in any other type of furnace can be economically melted in this elec. furnace; scrap metal can be repeatedly remelted without the addition of fresh pig Fe, since in the elec. furnace there is no increase in S as is always the case with the cupola. A table shows analysis of 11 samples, *e. g.*, before melting: 2.21% Si, 0.021 S, 0.76 combined C, 3.20 graphitic C, 0.606 P, and 0.62 Mn; after melting: 2.18, 0.026, 0.55, 3.07, 0.600, 0.65; after holding in molten condition for 14 hrs.: 2.23 Si, 0.032 S, 0.55 comb. C, 2.98 graph. C, 0.610 P, 0.63 Mn; after adding 642 lbs. of borings: 2.11, 0.047, 0.55, 2.60, 0.590, 0.60. C. G. F.

Electric muffle furnace for laboratory use. H. C. KREMERS. *J. Ind. Eng. Chem.* **13**, 561(1921); 2 illus.—An elec. furnace muffle and elec. conbustion furnace are described which use nichrome wire as resistor. Alundum cement is shaped around a bottle as a mold which is removed when the furnace is first heated. The unit is packed intc a container of Sil-o-cel. The muffle operates satisfactorily at 950°. E. M. ANGER

Electrolytic refining of tin in sodium sulfide solution. BERNHARD NEUMANN. Techn. Hochschule, Breslau. *Z. Elektrochem.* **27**, 256–68(1921).—It has been found that in the refining of Sn in Na_2S soln., the metal separates at the cathode as a smooth, dense deposit with a current-yield of 98–99% (calcd. with reference to tetravalent Sn), when a c. d. of 1 amp. per $dm.^2$ is employed. With a c. d. of 2 amps. or more, evolution of H occurs, the deposit of Sn on the cathode is spongy and the current-yield falls. The Na_2S content in the electrolyte must not be allowed to fall below 10%; otherwise a spongy deposit of Sn is formed. In Na_2S solns. containing NaOH the current yield is over 100%, owing to the discharge of some Sn^{++} ions. Free S in the electrolyte forms polysulfide, which dissolves the Sn and hinders its deposition. Initially the electrolyte

must contain at least 0.6% Sn, dissolved as SnS_2. The temp. of the electrolyte should be maintained above 80°; below 70° evolution of H sets in and the cathode becomes coated with a grey-black, spongy deposit. With anodes of alloys of Sn with Pb, Fe, Bi, Ag, Cu and P, these metals are converted into sulfides which settle as anode slime, the Sn deposited on the cathode being completely free from them. As is not deposited with the Sn on the cathode, but Sb is, if the c. d. is over 0.1 amp. per dm^2. Some expts. on the techn. refining of Sn have been carried out using as anodes South American crude Sn. H. JERMAIN CREIGHTON

Researches on the electrodeposition of iron. W. E. HUGHES. *Trans. Am. Electrochem Soc.* **40**, 40 pp. preprint(1921).—In this comprehensive and detailed paper H. considers the electrodeposition of Fe from the following solns.: (1) Sulfate solns: Of the 7 described, Klein's, using $FeSO_4$ as the metal salt and $MgSO_4$ as the conducting salt, is most favored for general uses; the results of MacFadyen (*C. A.* **14**, 498) are discussed. (2) Chloride solns.: The Fischer-Langbein, of 450 g. $FeCl_2$. *aq.*, 500 g. $CaCl_2$, and 500 g. H_2O, "proved to be one of the best Fe-depositing solns. available." (3) Sulfate-chloride solns.: The bath of Burgess, contg. 40 g. Fe per l. as $FeSO_4$, and 40 g. NH_4Cl was found most satisfactory. The general researches of many investigators are noted with comments, complete references being given throughout. The work of Russ and Bogomolny (*Z. Elektrochem.* **12**, 697) is most promising both with sulfate and chloride solns. H. points out that (1) ferrous salts alone are suitable, (2) the use of org. salts or addition agents is unnecessary, (3) the object for which the electrodeposit is required must govern the choice of electrolyte, (4) long experience indicates that slight acidity is beneficial, at least for sulfate baths, and (5) the sulfate bath permits a lower temp. and gives a more rust-resisting deposit than the chloride, though the latter enables a higher c. d. and a lower voltage to be used; the "mixed" electrolytes are difficult to control. F. H. HOTCHKISS

New type of electrolytic cell. HIRAM S. LUKENS. *J. Ind. Eng. Chem.* **13**, 562 (1921); 2 illus.—A type of electrolytic oxidation and reduction cell with mechanical agitation is described. This type of cell is very satisfactory for suspensions in electrolytes as it tends to promote a very uniform cond. in all parts of the cell, thus decreasing to a minimum the voltage drop. The cell has been tried out on such products as nitrobenzene, benzene and toluene, and anthracene in suspension in thin electrolytes, as well as on products which are sol. The cell is made up with an inner electrode of perforated stamped sheet metal. This inner electrode is placed in a porous cell and is fastened to a Pb plate cover through which the stirrer rod passes. Arrangement is also made for the study of efficiency at different c. ds. E. M. ANGER

The present status of the problem of combustion cells. EMIL BAUR AND W. D. TREADWELL. Zürich. *Brennstoff Chem.* **2**, 145–7(1921); *Z. Elektrochem.* **27**, 199–208 (1921).—The numerous attempts from the time of Grove (1843) to the present to construct an efficient combustion cell are reviewed, and the difficulties outlined. The producer-gas cell which is the subject of Ger. pats. 325,783 and 325,784(1920), Eng. pat. 126,766(1919), by Baur and W. D. Treadwell, is described. It is of the type, air electrode | salt-impregnated diaphragm | combustible gas electrode. The diaphragm is a prismatic structure of fritted MgO, containing channels filled with the active material, magnetite grains for the air electrode, fine iron wire for the combustible gas. The magnesia block acts as a wick for the melt of $Na_2CO_3+K_2CO_3$, the whole app. being maintained at a temp. of 800°. Cells of this type are said to give nearly the full reversible potential, to polarize only slightly, and not to deteriorate noticeably. The capacity is about 1 kw. per cu. m. In order to keep the heat loss low, the units must be of large size, say 10 m. on a side (=1000 kw.), to realize about 80% heat economy; and regenerative heating of the gases is necessary. The gases are only 70–80% burned, so

that the waste gases must be utilized. Under these conditions, about 60% of the heat of the coal would be recovered in useful form. W. B. V.

The luminous arc lamp. R. B. HUSSEY. *Gen. Elec. Rev.* **24**, 729–33(1921).—A review including essential information regarding the character of the arc, types of electrodes, operating features and the quality of light of luminous arcs. C. G. F.

Recent developments of the quartz tube mercury lamp. M. LE BLANC. *Bull. soc. franc. électriciens* [4] **1**, 89–95(1921).—Review of developments since 1914. C. G. F.

Phillips (neon) night lamp. ANON. *Electrician* **87**, 25(1921).—An interesting elec. night lamp has been placed on the market in England. It consists essentially of a spiral about $1^1/_2$" long and 1" in diam., which is arranged vertically in a bulb filled with Ne gas. Light is produced by a discharge from this spiral in a way similar to the Moore light or Hg vapor lamp, and the resulting illumination is of a beautiful orange color with a soft rich effect. The rating of the lamp is about 5 w. and its life is said to be considerably greater than that of the ordinary metal filament lamp. It is supplied for a. c. circuits from 110 v. upwards, and for d. c. circuits from 150 v. upwards. Lamps of this kind should find a useful application in hospitals, etc., where at present it is difficult to obtain the necessary reduced elec. illumination without an expenditure of an exorbitant amt. of energy. D. MACRAE

Effect of electron emission on the temperature of the filament and anode of a thermionic valve. G. STEAD. *Electrician* **86**, 755–6(1921).—In ordinary W incandescent lamps the filament is cooled by the evapn. of electrons from its surface. If in a thermionic valve the high potential battery is connected between the anode of a valve and the negative end of the filament, a current, a little smaller than the emission current, must traverse the negative limb of the filament in the same direction as the filament current, and the filament is heated by this in addition to the current supplied by the filament battery. The net result of these 2 effects is an unsymmetrical distribution of temp. along the filament, the temp. being higher in the negative limb than in the positive. Curves are given which show that the temp. at any point along a filament emitting electrons is higher than when the filament is not emitting electrons. An investigation of the dissipation of energy by a cylindrical anode of *Ni* shows that it varies from about 2 watts per sq. cm. at 1200° K. to 6 at 1600° K. D. MACREA

Some features of the Cottrell plant at the Hayden Smelter. C. G. HERSHEY AND R. B. RATHBUN. *Elec. J.* **98**, 304–6(1921).—The Cottrell precipitator at Hayden, Arizona, is a radical departure from the usual type in that the positive electrodes consist of a series of vertical pairs of grounded wire screens, and the negative electrodes are uniformly spaced wires placed between each pair of screens. The gas travels at right angles to the plane of the screens. This type of precipitator was developed by R. B. Rathbun. The precipitator is being operated solely to recover the Cu content of the roaster gases, which otherwise would be lost, and tests have shown the recovery to be but slightly less than 100%. A complete description of the construction and operation of the precipitator is given. C. C. VAN VOORHIS

Lightning arresters. ALFRED STILL. *Elec. Rev.* (Chicago) **79**, 192–6(1921); 4 illus.—A general survey. There are paragraphs on the electrolytic Al cell arrester, the oxide film arrester, water jet arresters, the Mosciki condenser, and corona as a protection against over-voltage. C. G. F.

Experiences with aluminium for electrical purposes. WUNDER. *Z. Metallkunde* **13**, 179–84(1921).—A questionnaire was sent to the users of cond. wire in German factories and power stations asking for information concerning the good and bad qualities of Al wire and cable. The results are tabulated and though some of the replies indicated difficulties, the great majority of the users had had satisfactory results. R. S. WILLIAMS

English oil-break switches for low voltage circuits. ANON. *Elec. Rev.* (Chicago) 79, 191(1921). C. G. F.

The absolute measurement of resistance (GLAZEBROOK, SMITH) 2. Tungsten-zirconium alloys; electric filaments (BRIT. pat. 162,907) 9. Making tungsten wire (BRIT. pat. 163,014) 9.

LUMMER, OTTO: **Grundlagen, Ziele und Grenzen der Leuchttechnik.** München and Berlin: Verlag R. Oldenbourg. M 25. For review see *Chem. Weekblad* **18**, 407(1921).

Electric furnaces. MORGAN CRUCIBLE CO., LTD and C. W. SPIERS. Brit. 162,246, Oct. 7, 1919. Resistance tubes or crucibles are sepd. from a refractory outer wall by natural graphite in the form of flakes, which may be got by grinding the graphite and freeing it from dust; graphite of high C content should be used. Such flaky graphite, if loosely packed, has low elec. and thermal conductivity and is sufficiently elastic to allow expansion and contraction of the crucible, etc. Around the cooler part of the crucible, from the bottom terminal to a point within the casing, there may be placed a fine powder, such as sand or finely ground earthenware, to insulate the graphite from the terminal.

Automatic temperature control device for electric furnaces. A. L. WILKES. U. S. 1,377,952, May 10.

Melting oxides without contamination. E. F. NORTHRUP. U. S. 1,378,189, May 17. In melting oxide of Al, B, Th or Mg or similar materials, in an elec. heated furnace, a crucible is used which is formed of an oxide, *e. g.*, of Ti or Zr, having a m. p. above the temp. required for the furnace operation. The crucible contains a body of molten metal the oxide of which is to be melted.

Carbon electrodes. W. G. MICHEL. U. S. 1,378,599, May 17. Electrodes adapted for use in chem. work are formed of pulverized dry C with a hydrocarbon binder mixed with the C by vacuum and pressure and baked to a solid mass.

Apparatus for electrostatic precipitation of suspended matter from gases. G. KRAUSE. U. S. 1,377,205, May 10.

Apparatus for electrically precipitating suspended particles from gases. C. W. GIRVIN. U. S. 1,378,224, May 17.

Electric discharge apparatus. NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIEKEN. Brit., 162,268, Feb. 18, 1921. To facilitate the starting of a lamp Mg, Be, or Tl or alloys thereof are combined mechanically with, or alloyed with the usual material of the electrodes, for instance Fe or Al. The electrode may be formed as a cap-shaped enclosure around the Mg, etc. to prevent too great vaporization, or a mica screen may be provided on which the vaporized metal is deposited. Cf. *C. A.* **15**, 1835.

Electric battery. A. P. MANCHESTER and H. M. SPOONER. U. S. 1,378,549, May 17. Battery electrodes are formed of CuO, Cu_2O and the residue of a saccharine binder, *e. g.*, sugar.

Electric rocking furnace adapted for melting zinc. E. F. COLLINS. U. S. 1,378,526, May 17.

Depolarizing material for dry cell batteries. J. W. WEISS. U. S. 1,377,645, May 10. A depolarizing material for dry cells is prepd. by violently agitating powdered carbonaceous material and powdered MnO_2 together with an excess of H_2O and then sepg. the excess H_2O.

Storage battery. T. A. EDISON. U. S. 1,377,194, May 10. A storage battery is formed with alternately disposed positive and negative elements each comprizing a

conductive metallic foil such as Ni and active material, *e. g.*, active Fe and Hg, maintained under pressure in firm contact with the metallic foil.

Storage battery. G. MARCONI. U. S. 1,377,722, May 10. See Brit. 151,293 (*C. A.* **15**, 473).

Storage battery. T. SPENCER. U. S. 1,377,227, May 10. Structural features.

Storage battery. T. A. WILLARD. U. S. 1,377,995, May 10. Structural features.

Diaphragms for electrolytic cells. C. N. RIBER. U. S. 1,378,829, May 17. A diaphragm suitable for use in cells for the electrolysis of alkali metal chloride solns. is formed of metal netting carrying pulverulent fibrous material such as asbestos, applied to the netting without an agglutinant, from a suspension in liquid.

Electrodeposition of copper. F. E. STUDT. U. S. 1,378,145, May 17. In the electrolysis of acid $CuSO_4$ solns., anodic polarization in a Cu-depositing cell is prevented by the cyclic operation of introducing an amount of SO_2 into the soln. at the anode capable of forming H_2SO_4 in the soln. in excess of that required for leaching ores, utilizing a portion of the H_2SO_4 thus formed for leaching Cu ore material, conveying the soln. to the cell, and decomposing another portion of the H_2SO_4 by heating it with S to produce SO_2 which is used for continuation of the first mentioned step of the process.

Permanganates. H. C. JENKINS and H. WOOLNER. U. S. 1,377,485, May 10. $KMnO_4$ is prepd. by the following process. MnO_2 is fused with an excess of NaOH at a dull red heat with the employment of an oxidizing agent such as $NaClO_3$, the melt is dissolved and the soln. is sepd. from residual mud and electrolyzed to form permanganate. A K compd., *e. g.*, KCl, is then added to the permanganate soln. to form $KMnO_4$ and the Na compds. are reused in the continuation of the first part of the process.

Boron manufacture. G. CONSTANT and V. RAISIN. Brit. 162,252, Apr. 22, 1921. B is produced by electrolysis of fused boric acid made conductive by the addition of a suitable substance such as borax. Both electrodes may be metallic or the anode may be of retort carbon. CO and CO_2 formed in the latter case assist in the operation. The process is carried out in a closed vessel having an outlet pipe for gases. The vessel may be of insulating material or of metal and in the latter case forms the cathode. The cables pass through the wall of the vessel or through the cover. B so produced may be used as a reducing agent in metallurgy.

Manufacture of boron. G. CONSTANT and V. RAISIN. Brit. 162,655, Apr. 26, 1921. Addition to 162,252 (preceding abst.). B is obtained by electrolysis of a mixt. of fused boric acid with a saline or basic electrolyte such as NaCl or an alkali borate. The boric anhydride itself may be replaced by an alkali or other fusible borate or mixt. of borates.

Electrifying substances prior to their chemical reaction. J. E. BLOOM. U. S. 1,377,553, May 10. Reactions between different solids, such as C and Na_2CO_3 in making NaCN, or between solids and gases as in the reaction of N on carbide, are facilitated by pulverizing the solids under insulated conditions while giving them elec. charges of opposite signs, before the reaction, or by similarly separately electrifying the gas and solid in the case of reactions of gases on solids.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Optically active cobalt salts with β-diketone radicals in the complex. A. WERNER, J. E. SCHWYZER AND W. KARRER. *Helvetica Chim. Acta* **4**, 113–29(1921); cf. *C. A.* **12**, 1863.—The action of Ac_2CH_2 or $EtCOCH_2Ac$ on optically active chloroaquodiethylenediamine Co salts gives active products, the active chloro-aquo salts being

obtained by resolving the *d,l*-series by means of bromocamphorsulfonates. A filtered soln. of 150 g. of *d,l*- 1,2-chloro-aquo-diethylenediamine-cobaltibromide and 135 g. of ammonium *d*-α-bromocamphor-π-sulfonate is cooled with ice and rubbed with a glass rod, until after about 45 mins. the *l*-salt seps. After the mass has solidified, 100–250 cc. of ice H_2O are added, the crystals filtered off, washed with a little ice H_2O, and the pink crystal cake is rubbed with 170 cc. of HBr (d. 1.48), giving a cryst. mass of the glittering dark violet *l*-bromide. This was filtered off, dissolved in H_2O below 40° in the proportions of 1:5 ,and $^1/_3$ of its vol. of HBr added, cooling with ice. The *l*-bromide thus purified and washed with EtOH is usually pure, a 1% soln. having $[\alpha]_D$ −214°. The filtrate from the *l*-salt is then treated with $^1/_3$ its vol. of HBr (200–250 cc.), which throws out the *d*-bromide after a time, which is filtered off and purified as above, then having $[\alpha]_D$ 214°. The yield of each form is 35–40 g. Three g. of the *d*- or *l*-bromide are treated with 6 cc. of 10% KOH, which dissolves the salt with a reddish violet color, 1.5 cc. of Ac_2CH_2 in 4 cc. of EtOH are added, the soln. is warmed to 40°, and the filtered soln., which has a deep orange-red color, treated with 5 g. of powdered KI. The brilliant red iodide is filtered off and dried on porous tile; a larger yield can be obtained by satg. the filtrate again with KI. Yield, 4–5 g. of iodide, containing small amts. of *d,l*-salt, which is removed by dissolving the salt in a little boiling EtOH, filtering quickly, and cooling slowly, giving *d*- or *l*-*acetylacetonato-diethylenediamine cobalti-iodide*, thin red prisms with 1 H_2O, easily sol. in H_2O and Me_2CO, less sol. in EtOH, $[\alpha]_D$ ±400° in 0.1% soln., $[M]_D$ ±2204°. *Chlorides*, from the iodides in abs. EtOH by the action of excess dry AgCl and pptn. with Et_2O, fine brilliant red needles, very deliquescent until all traces of solvents are removed; contains 1 H_2O, $[\alpha]_D$ 543° or −550°, $[M]_D$ 2107 or −2134°. *Bromides*, from concd. solns. of the active chlorides by double decompn. with KBr, bright red cryst. ppt., or thin red prisms from EtOH, with 1 H_2O, $[\alpha]_D$ 460°, $[M]_D$ 2102°. *Thiocyanates*, small bright crystals, with 2 H_2O, very easily sol. in H_2O, EtOH and Me_2CO, $[\alpha]_D$ 533°, $[M]_D$ 2107°. • *Perchlorates*, fine red prisms, without H_2O, soly. like the bromides, $[\alpha]_D$ 543°, $[M]_D$ 2107°. • *Persulfates*, fine red crystals from 60% EtOH, $[\alpha]_D$ 433° or −480°, $[M]_D$ 2040° or −2261°. *Nitrates*, from the active iodides in abs. EtOH and $AgNO_3$ and pptn. with Et_2O, beautiful red needles, deliquescent until all solvent is removed, containing no crystal H_2O, easily sol. in H_2O, EtOH and Me_2CO, $[\alpha]_D$ 550°, $[M]_D$ 2217°. By treating 10 g. of *d,l*-chloro-aquo-diethylenediamine-cobalti-bromide in 20 cc. of 10% KOH and 15–20 cc. of H_2O, with 3 g. of $EtCOCH_2Ac$ [prepd. by the method of Claison and Ekehardt, *Ber.* **22**, 1009(1889)] in 20 cc. of EtOH, and adding 10 g. of powdered KI to the filtrate warmed to 40°, *d,l-propionylacetonato-diethylenediamine-cobalti-iodide* is pptd. and obtained pure by recrystn. from hot H_2O, forming well-shaped prisms containing 1 H_2O; 100 cc. of H_2O dissolve 2.1 g. at 15° and 21 g. at 60°. *Bromide*, by the action of freshly pptd. AgBr on the iodide in a little warm H_2O, and concg. red crystals with 1 mol. of H_2O; *chloride*, from the iodide and AgI, imperfect red crystals, very easily sol. in H_2O; *nitrate*, from the iodide and $AgNO_3$, large red crystals; *sulfate*, from the iodide and Ag_2SO_4, long red needles, anhydrous; *thiocyanate*, small red crystals; *perchlorate*, from a soln. of the chloride and $NaClO_4$, well formed red crystals, anhydrous; *persulfate*, small orange red needles, with low soly. The reaction mixt. described above, on treating with 5 g. of KI, gives a ppt. containing chiefly hydroxo-aquo-diethylenediamine salts, which are filtered off and rejected. The further addition of 5 g. of KI gives a ppt. of *d,l*-propionylacetonato-iodides, which are removed, and the filtrate is allowed to stand at room temp., crystals being removed after 1, 2, 4, and 6 days, the remainder after 3 weeks. Fractions showing approx. the same $[\alpha]$ are then united and refractionated from H_2O, finally yielding large red prisms of the pure active *propionylacetonato-diethylenediamine-cobalti-iodides*, containing 1 H_2O, $[\alpha]_D$ 465° or

$-434°$, $[M]_D$ 2623° or $-2448°$; after 4 months $[\alpha]_D$ sank to 402° and $-390°$. *Nitrates*, well formed anhydrous crystals, $[\alpha]_D$ 596° or $-591°$; $[M]_D$ 2481° or $-2460°$; somewhat lower after 4 months. *Perchlorates*, from the iodides and freshly pptd. AgCl, giving a soln. of the chlorides, which was treated with $NaClO_4$, anhydrous red crystals, $[\alpha]_D$ 504° or $-496°$, $[M]_D$ 2476° or $-2436°$. *Perchlorates*, difficultly sol. orange-red anhydrous needles, $[\alpha]_D$ 477° or $-492°$, $[M]_D$ 2311° or $-2383°$. The iodides show an abnormal rotation-dispersion curve, with a max. at wave length 554$\mu\mu$.

M. R. SCHMIDT

Residual affinity and coördination. V. Gallium acetylacetone and its analogs. GILBERT T. MORGAN AND HARRY D. K. DREW. Univ. Birmingham. *J. Chem. Soc.* **119**, 1058–66(1921).—*Gallium acetylacetone*, $C_{15}H_{21}O_6Ga$, is best prepd. by the action of $Ga(OH)_3$ upon $AcCH_2COMe$, and exists in 2 forms, *α-form*, monoclinic, isomorphous with the Al compd., and *β-form*, orthorhombic, isomorphous with the β-form of the In compd., m. 194–5°. Crystallographic measurements are given for the three (Al, Ga, and In), and also comparative reactions. The Ga salt falls between Al and In, because of the manifestation of dimorphism and because of its chem. properties. **VI. Selenodithionic acid and its metallic salts.** GILBERT T. MORGAN AND J. D. MAIN SMITH. *Ibid* 1066–70.—$(Se:C_5H_6O_2)_2$ (A) reacts with $RHSO_3$ or R_2SO_3 to give the corresponding R selenodithionate. (Cf. *C. A.* **15**, 1493.) *Lithium salt*, $Se(SO_3Li)_2.3H_2O$, from 7 g. A and 5.2 g. $Li_2SO_3.2H_2O$ in 45 cc. 2 *N* H_2SO_3, colorless hexagonal plates, which rapidly deliquesced in air and decompd. with liberation of red Se. *Sodium tetrahydrate*, $Se(SO_3Na)_2.4H_2O$, from 7 g. A and 9 g. $NaHCO_3$ in 30 cc. H_2O, purified by pptn. from hot H_2O with EtOH, prismatic needles which gave up its H_2O in a dry atm. *Rubidium salt*, $Se(SO_3Rb)_2$, from 1.8 g. A and 3.6 g. $RbHSO_3$ in 10 cc. H_2O, small needles. *Cesium salt*, $Se(SO_3Cs)_2$, filamentous needles from hot, dil. alc., and transparent tubular prisms from H_2O. This salt has the greatest capacity for crystg. of all the salts examd. *Ammonium selenodithionate*, $Se(SO_3NH_4)_2$, colorless needles which rapidly redden on exposure to air. *Barium salt*, $Se(SO_3)_2Ba.2H_2O$, needles, which redden on prolonged exposure. The Cd salt could not be obtained because of its great soly. *Rubidium hydrogen sulfite*, $RbHSO_3$, by passing SO_2 into a soln. of Rb_2CO_3 until a pale green tint was assumed, was pptd. by alc. as prisms, readily sol. in H_2O, gave an acid reaction with litmus and phenolphthalein but was neutral to Me orange. *Rubidium sulfite*, by adding the carbonate to the acid sulfite, eliminating the CO_2 by heating and pptg. with alc. as the *alcoholate*, $2Rb_2SO_3.EtOH$, from which the anhydrous salt was obtained by concg. an aq. soln., small, prismatic tablets, sol. in H_2O and dil. alc., strongly alk. to litmus, evolved SO_2 with dil. mineral acids. The reactions of the selenodithionates are tabulated.

C. J. WEST

Influence of double bonds on the coördination number. A. PIERONI. Univ. Bologna, *Gazz. chim. ital.* **51**, I, 42–7(1921).—Previous work on the salts of Ni and allylamine (*C. A.* **9**, 1041) gave products which were not suited to study as complex salts. Werner's theory for the formation of these complexes which permits of many predictions and many results is also faced by many contradictions. In fact perfect compds. fitting W.'s theory are exceptional. When any compd. is dissolved it is bound to the mols. of the solvent and if insol. complexes are formed these sep. This universal process is analogous to the formation of complex salts. Moreover, if complex mols. may be formed between different mols. they may be formed among mols. of the same kind. The force that leads to the formation of complex salts and polymers ought to be in some ways similar to and in some ways different from that generally considered as detg. the residual valence. The mol., even if satd. with respect to valence, ought to have a different chem. potential, and to this difference the formation of complexes may be attributed. This supposition has as a consequence that if a compd. is sol.

in a given solvent the difference in potential that holds the polymeric mols. of a kind together is less than the differences of potential existing between this and that of the solvent. By varying the reagents, the conditions or the solvent the coördination no. may be changed. On the basis of such ideas the solvent should have an influence upon the coördination no. and P. has undertaken the study of the influence of an amine containing an unsatd. bond upon this no. by allowing Cr and Co salts to react with allylamine. The definite compd. $Co(C_3H_5NH_2)_6O_6Cl_3$ (A) was obtained by suspending $CoCl_2.3C_3H_5NH_2$ in abs. EtOH and $C_3H_5NH_2$ distd. over Na and oxidizing with a slow current of dry air. A is a red cryst. substance that decomps. at 120–40° without melting and gives a neutral soln. in H_2O, but on boiling becomes alk. and on addition of KOH ppts. $Co(OH)_2$ after a time. A may be considered to be the peroxide $Co(CH_2.O.CH.CH_2NH_2)_6Cl_3$, since it frees I from KI and reduces $KMnO_4$ rapidly and thus is analogous to the known peroxides $Co_2O_2(NH_3)_{10}X_4.MH_2O$ and $Co_2O_2(NH_3)_{10}Cl_5$. On the other hand the I_2 liberated could not be detd. and the $KMnO_4$ results seem to indicate that but one O atom is combined as indicated and for this the alternative formula $Co\begin{pmatrix}(C_3H_5NH_2)_6\\2O_2\end{pmatrix}Cl_3.H_2O_2$ is given. Other reactions could not be tried owing to the lack of materials. Although this complex shows an anomalous coördination no. of 8, P. does not wish to draw further conclusions until more data are obtained. Seven cc. of abs. EtOH satd. with $CoCl_2$ in a dry beaker with 10 cc. dry $C_3H_5NH_2$ sepd. $CoCl_2.3C_3H_5NH_2$ on cooling as reddish needles. Other compds. of Co and Cr are mentioned but not described.

E. J. WITZEMANN

Thallous ferricyanide. V. CUTTICA AND G. CANNERI. R. Ist. di Studi Superiori, Florence. *Gazz. chim. ital.* 51, I, 169–74(1921).—Carstanjen (*J. prakt. Chem.* **102**, 144(1867)) failed to obtain thallous ferricyanide (A) by adding $K_3Fe(CN)_6$ to thallous salt. Fischer and Benzian (*Chem. Ztg.* **26**, 49(1902)) first tried to obtain A by oxidizing thallous ferrocyanide with Cl and Br as was done with $K_4Fe(CN)_6$ and $Ba_2(Fe(CN)_6)_2$, but obtained Tl halides and Tl_2O_3. On treating Tl_2SO_4 with $K_3Fe(CN)_6$ they obtained $K_2TlFe(CN)_6$. Using Tl_2HPO_4 they obtained $Tl_3KFe_2(CN)_{12}$. Other prepns. for which formulas could not be calcd. are according to C. and C. probably isomorphous mixts. of $K_3Fe(CN)_6$ and $Tl_3Fe(CN)_6$. Concd. solns. of Tl′ salts with $K_4Fe(CN)_6$ sep. $Tl_4Fe(CN)_6$ as a yellow powder. The aq. soln. of this salt treated with dil. acid becomes blue-green and on addition of alkali yellow again. When heated to 100° it becomes green. This green form behaves like the yellow form with acid and alkali. Apparently there are 2 isomeric forms of $Tl_4Fe(CN)_6$ as Briggs (*C. A.* **5**, 3018) found for $K_4Fe(CN)_6$, $(NH_4)_4Fe(CN)_6$, etc. The soly. of $Tl_4Fe(CN)_6$ is increased by $K_4Fe(CN)_6$ and crystals always contain $K_4Fe(CN)_6$, indicating that here too there is a series of solid solns. On account of the isomorphism of K and Tl recourse was had to a double decompn. reaction using $Ag_3Fe(CN)_6$ and $Pb_3(Fe(CN)_6)_2$. In a soln. of TlCl a slight excess of $Ag_3Fe(CN)_6$ was suspended. The mixt. was heated, the AgCl sepd. and the soln. on concn. *in vacuo* over H_2SO_4 sepd. shining black crystals of A (red-brown under the microscope), which are very sol. in H_2O. $Pb_3(Fe(CN)_6)_2$ prepd. from aq. solns. of $Pb(NO_3)_2$ and $K_3Fe(CN)_6$ as $Pb_3(Fe(CN)_6)_2.Pb(NO_3)_2.10H_2O$, treated with 4 mols. Tl_2SO_4 gave $PbSO_4$ and a soln. of A and $TlNO_3$, from which $TlNO_3$ sepd. first on crystg. A reacts with KOH thus: (1) $Tl_3Fe(CN)_6 + 3\ KOH \rightarrow 3TlOH + K_3Fe(CN)_6$; (2) $4\ K_4Fe(CN)_6 + 4\ KOH + 2TlOH \rightarrow 4\ K_4Fe(CN)_6 + Tl_2O_3 + 3H_2O$. A with inorg. acids evolves HCN. With dil. acids and alkalies, A shows green and yellow colorations, resp. A soln. of $Tl_4Fe(CN)_6$ treated with H_2O_2 became yellow and gave the red-brown crystals of A. The gravimetric and volumetric methods of detg. Tl were both used. Of these the latter was not quite so accurate but was rapid;

it was carried out as follows: The soln. to be titrated should contain enough Tl to form about 0.2 g. Tl_2CrO_4; it is pptd. with a known excess of alkali chromate and filtered off. The ppt. is washed with 80% EtOH until free from sol. chromate reaction. It is then dissolved in 100 cc. 2.0 *N* H_2SO_4, dild. to 400 cc., treated with 2 g. KI and titrated with 0.1 *N* $Na_2S_2O_3$ with starch as indicator. E. J. WITZEMANN

The double phosphate of iron and sodium. E. OLIVERI-MANDALÁ. Univ. Palermo. *Gazz. chim. ital.* **51**, I, 130–7(1921).—Fe'' and Fe''' form complexes with many substances which vary widely in stability. Since 1847 it has been known that heavy metal pyrophosphates are easily sol. in alkali pyrophosphate solns., in which they do not give tests for these metals. The pyrophosphate of Fe and Na (A), which has been prepd. frequently, is not well crystd. and is variable in compn. Because of its therapeutic importance it was studied in detail. Pahl's (*Bull. soc. chim.* **19**, 115(1873)) formula of A was found to be wrong; $Fe_4(P_2O_7)_3.3Na_4P_2O_7.14H_2O$, the one usually given in pharmaceutical chemistry, was confirmed. The usual method of prepn. was improved as follows: Solns. of $Na_4P_2O_7$ are agitated mechanically with fresh wet $Fe_4(P_2O_7)_3$ and when the soln. is satd. with the Fe compd. the double salt is pptd. with EtOH. In this way the presence of NaCl was excluded, which it seems impossible to wash out. The Fe was detd. by dissolving the complex in 30% H_2SO_4, reducing with H_2S, removing free H_2S and titrating with $KMnO_4$. Solns. of A in alkali citrates were first evapd., calcined cautiously and then treated as above for analysis. From data on the soly. of $FeCl_3$ in $Na_4P_2O_7$ O.-M. concludes that the ratio for $Fe_4(P_2O_7)_3 : Na_4P_2O_7$ should be 1:3. Soly. detns. with $Fe_4(P_2O_7)_3.9H_2O$ (air-dried) in various dilns. of $Na_4P_2O_7$ gave the ratio 1:2.84, but with the fresh wet ppt. 1:2.98 was obtained. A is accordingly closely allied to the complexes of isopolyacids of Werner's classification such as the alkali bimolybdates, $M(Mo_2O_7)_3R_3$, in which M is Al, Cr or Co. $Fe_4(P_2O_7)_3$ is sol. in solns. of Na citrate of various concns. in the mol. ratio of 1:1 for the 2 salts. The soly. of A in Na citrate is small in comparison. The presence of NaCl diminishes the soly. of A in H_2O considerably and for this reason prepns. of A contg. NaCl must be washed thoroughly. E. J. WITZEMANN

Reaction between halogen cyanides and sodium thiosulfate. ALBIN KURTENACKER. *Z. anorg. allgem. Chem.* **116**, 243–9(1921).—The reaction was found to be analogous for both ICN and BrCN. In neutral soln. $3HalCN + 5S_2O_3'' + H_2O = 3Hal' + 2HCN + CNS' + SO_4'' + 2S_4O_6''$; in acid soln., $HalCN + 2S_2O_3'' + H^+ = Hal' + HCN + S_4O_6''$. Meineke (*Z. anorg. Chem.* **2**, 157(1892)) overlooked the formation of thiocyanate; Dixon and Taylor (*C. A.* **7**, 3120) were led to an erroneous equation through choice of unsuitable analytical methods. In neutral soln. reaction 2 is also the primary reaction and the soln. becomes alk. temporarily in consequence of formation of NaCN according to $3HalCN + 6Na_2S_2O_3 = 3NaHal + 3NaCN + 3Na_2S_4O_6$ but soon becomes neutral again in consequence of $3NaCN + Na_2S_4O_6 + H_2O = NaCNS + Na_2SO_4 + 2HCN + Na_2S_2O_3$. A. R. MIDDLETON

Metallic hydrides and action of hydrogen on the metals. E. TOMKINSON. *Chem. News* **122**, 241–3(1921).—A summary and bibliography of articles dealing with the hydrides of Ca, Ba and Sr. A. R. M.

Action of ammonium citrate on alkaline earth sulfates. MLLE. VIRGINIE TEODOSIU. *Bul. Soc. chim. România* **3**, 9–17(1921).—The solubilities of the sulfates of Ca, Sr and Ba in NH_4 citrate solns., 0.2, 0.1, 0.08 and 0.04 molar, were detd. at 20° and at 40° after periods of contact of 1, 3 and 6 hrs. The max. transformation of sulfate into citrate was found to be in 0.2 mol. soln. at 20° after 3 hrs. when about 50% of $CaSO_4$, 12% of $SrSO_4$ and 3% of $BaSO_4$ were transformed: 100 cc. soln. dissolved 2.59 g. $CaSO_4$, 0.68 g. $SrSO_4$, 0.21 g. $BaSO_4$. A. R. MIDDLETON

Experimental note on complex ion formation in hydrochloric acid. RALPH M.

HIXON. *Medd. Vetenskapsakad. Nobelinst.* **4**, No. 12, 8 pp.—Solns. of $MgCl_2$ and $CaCl_2$ in HCl (d. 1.19) were subjected to a p. d. of about 12 v. for 6–8 hrs. Both showed migration of metal toward the anode at medium concns. while both dil. and more concd. solns. showed migration toward the cathode. Ba and Zn in similar conditions migrated only toward the cathode. Formation of complex ions of the type $(Cl_x(MCl_2)_y)$ is assumed. A. R. MIDDLETON

Slaked lime and milk of lime. B. KOSMANN. *Z. Elektrochem.* **26**, 173–81(1920). The views of Kohlschütter and Walther (*C. A.* **15**, 1792) are criticized. K. holds the view that the slaking of lime consists in a gradual stepwise combination with water in which the following substances are produced in order: $Ca(OH)_2$,$HCa(OH)_3$, $H_2Ca(OH)_4$ $H_3Ca(OH)_5$, $H_4Ca(OH)_6$, $H_5Ca(OH)_7$, $H_6Ca(OH)_8$, and $H_7Ca(OH)_9$. J. S. C. I.

Slaked lime and milk of lime. V. KOHLSCHÜTER. *Z. Elektrochem.* **26**, 181–2 (1920).—An answer to Kosmann (preceding abst.). J. C. S.

The relation of structure to free alkali in sodium silicate solutions. WM. STERICKER. Mellon Inst. *Chem. Met. Eng.* **25**, 61–2(1921).—Ultramicroscopic examn. of sodium silicate solns. shows that they are 2-phase systems in which the disperse phase has a negative charge. This probably explains the discrepancies between detns. of the degree of hydrolysis by various methods. WM. STERICKER

A decomposition of nitrous acid. E. OLIVERI-MANDALÀ. Univ. Palermo. *Gazz. chim. ital.* **51**, I, 138–40(1921).—When NaN_3 or HN_3 is added to an aq. soln. containing an alkali nitrite and the mixt. acidified, a mixt. of equal vols. of N_2O and N_2 is evolved in accordance with the equation $HNO_2 + HN_3 \rightarrow H_2O + N_2O + N_2$. The soln. contains neither HNO_2 nor HNO_3 after the reaction is finished. It is supposed that the HNO_2 reacts first to give the unstable suboxide N_4O, which may be considered to be the unknown nitrosodiazoimide $N_2{:}N.NO$; this decomposes at once, giving $N_2 + N_2O$. This decompn. offers a method for the *detn. of HNO_2 in the presence of much HNO_3*, since unlike other available methods the decompn. of HNO_2 in this way does not give rise to HNO_3. This test for HNO_2 is preferred above that of Dey and Sen (*C. A.* **5**, 3391) using N_2H_4. The test is carried out as follows: To the soln. contg. HNO_3 and HNO_2 acidified with AcOH, in case the salts are present, several cc. of dil. soln. of HN_3 are added and then a little NaN_3. It is then boiled to drive out as much excess HN_3 as possible (because it interferes with the color tests for HNO_2 and HNO_3 with brucine, $C_6H_4(NH_2)_2$ or naphthylamine). After this heating a portion of the liquid is tested with the sensitive Ilosvay von Ilosva soln. (AcOH soln. of naphthylamine and sulfanilic acid) in order to det. if all HNO_2 has been removed. The soln. is then tested with the usual reagents for HNO_3. E. J. WITZEMANN

Water and ice. (LEBAS) **2.** Solubility of calcium sulfide in the presence of hydrogen sulfide (RIESENFELD, FELD) **2.**

LEWIS, E. I.: **Inorganic Chemistry.** 3rd revized & enlarged edition. Cambridge: University Press. For review see *Science Progress* **16**, 151(1921).

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Estimation of the hydrogen exponent with color indicator papers. I. M. KOLTHOFF. Utrecht. *Pharm. Weekblad* **58**, 961–70(1921).—Test papers may be used to estimate the p_H of very small amts. of soln. The method is accurate in most cases to about 0.2–0.4 p_H units. In general, hardened filter paper is best for making test papers

The drop should be transferred to the paper with a capillary tube delivering a known vol., and should not be dried before comparing with the standard. For most indicators the comparison should be made within 3–5 min. The buffer soln. should be sufficiently concd. to give a fairly large reaction spot in the center of the drop, but not concd. enough to interfere with the comparison. The method is not applicable to volatile acids, as H_2CO_3. The salt and albumin errors for each indicator are about the same on paper as in soln. Papers made from the following indicators were found applicable within the p_H ranges given: Congo 2.5–4.0; methyl orange 2.6–4.0; blue lacmoid 4.8–6.0; alizarin 4.6–5.8; metachrome red 6–8.5; brilliant yellow 6.8–8.0; red litmus 6.6–8.0; blue litmus 6.0–7.8; azolithmin 6–8.0; α-naphtholphthalein 8.2–9.5; curcuma 7.5–9.5. Hematoxylin, though not suitable for p_H detns., is applicable to strong acids. It is salmon in 0.5 *N* and rose red in 3–4 *N* acid. Litmus paper is especially suitable for use with colored substances such as wine, beer, urine, etc. Its relatively high salt and albumin error must be remembered in this connection. Methyl red, phenol red, neutral red and rosolic acid do not give good results on tests papers. The technic recommended by Haas (*C. A.* **13**, 2378) does not give the best results. Details of prepn. and use of test papers are given for the indicators listed.

JULIAN F. SMITH

Significance of adsorption in analytical chemistry. VI. Adsorption of lead and copper by filter-paper. I. M. KOLTHOFF. *Pharm. Weekblad* **58**, 152–9(1921); cf. *C. A.* **15**, 995, 1189.—Pb is not completely adsorbed from its solns. by filter-papers with low ash-alkalinity. If, however, the soln. is treated with NaOH soln. contg. carbonate, most of the Pb is pptd. and the remainder adsorbed, and on subsequently treating the filter with acetic acid, all the Pb is re-dissolved. This method may be applied to the estn. of Pb in drinking water, but a preliminary blank test for Pb in the filter paper must be made. For the quant. estn. the Pb in the soln., before and after adsorption, is pptd. as sulfite and collected on asbestos. The ppt. is then oxidized with Br, and excess of the latter detd. iodometrically. With high concns., adsorption is proportional to the alkalinity of the filter ash, and to remove Pb entirely from its solns. by means of filter-paper or cotton wool, these must have a high alkalinity; no appreciable quantities of Pb are adsorbed when the ash-alkalinity is negligible. Adsorption of Cu by filter-paper is very slight, and bears no relation to the alkalinity of the ash. From solns. in distd. water, more Cu is adsorbed than from solns. to which Na_2CO_3 or NH_3 is added. From dil. ammoniacal solns. of Cu more is adsorbed than from those of higher concn. In contradistinction to that of Pb, the adsorption of Cu from neutral solns. is negligible, but from solns. in NH_3 a high adsorption takes place.

J. C. S.

Significance of adsorption in analytical chemistry. VII. Adsorption of silver, mercury and other metals. I. M. KOLTHOFF. Utrecht. *Pharm. Weekblad* **58**, 233–41 (1921); cf. preceding abst.—From expts. with various salts of Ag, Hg and Fe it is concluded that these metals are not adsorbed in the physical sense. Their ions, and H^+, are taken up by cotton and by filter paper; but this is due to chem. interchange of ions with the inorg. part (ash) of the fiber. The effect is that of replacing Ca or other metal in a permutite by H^+, Hg^{++}, Fe^{++} or Fe^{+++}. This accounts for the widespread error of stating that cellulose acts as an acid in combining with metal oxides. The equil. concns. for the various ions with cellulose are not known. **VIII. Adsorption by asbestos.** *Ibid* 401–7.—Expts. with salts of Ag, Pb, Cu, Ni and Fe showed that impure asbestos, which is hygroscopic, tends to adsorb metal ions. Com. asbestos should always be tested. It should not take up more than 0.1 cc. of 0.1 *N* acid per g. when shaken 1 hr. with dil. acid. Asbestos which takes up no acid will not adsorb metal ions. To purify com. asbestos, ext. repeatedly with boiling HCl. The adsorption of H^+ or metal

ions follows the adsorption isotherm. Traces of Pb^{++} may be removed quant. from potable waters by use of impure asbestos. **IX. Glass wool as a filter medium.** *Ibid* 463–71.—Glass wool is attacked much more rapidly by HCl than by H_2O or dil. alk. The effect increases with increasing concn. of HCl. At room temp. salts of metals and alkaloids are taken up only very slowly; but the effect is greatly increased by higher temps. It is also dependent on the concn. of the salt. Glass wool should not be promiscuously used for filtration; its alk. nature may affect certain substances, and its adsorbing properties become quite appreciable with hot or concd. solns. The expts. were made with H_2O and HCl and with salts of Pb, Cu, Zn, NH_3, Ag, quinine and morphine. Two kinds of glass wool were used: one from Jena and one from an ordinary com. glass. JULIAN F. SMITH

Quantitative separation of arsenic, antimony and tin. FRIEDRICH L. HAHN AND PETER PHILIPPI. *Z. anorg. allgem. Chem.* **116**, 201–5(1921).—Some 53 analyses with widely varying quantities of As, Sb and Sn, show that excellent results can be obtained by starting with the sodium thio salts of these elements, pptg. the Sb as pyroantimonate by treatment with NaOH and H_2O_2, the Sn as metastannic acid by boiling with NH_4NO_3 and the As as $MgNH_4AsO_4$. Such a sepn. was always spoiled in the past by the addition of tartaric acid when the thio salts were oxidized by H_2O_2 as in the Henz modification of F. W. Clarke's method for sepg. Sb and Sn. The procedure is as follows: Dissolve the mixed sulfides, as ordinarily obtained by treatment with H_2S, in as little 10% Na_2S soln. (to which a little NaOH has been added) as possible. Add the reagent from a graduate and use about 2 cc. for each 0.1 g. of As, Sb, or Sn. Add an equal quantity of 20% NaOH (more rather than less), dil. to 50–100 cc., and add in small portions strong H_2O_2 soln. (10–30%) with stirring. The soln. should assume a temporary light-yellow color. If a brown color results, more alkali should be added. Finally complete the oxidation of the thio salts by heating on the water-bath. Allow the liquid to cool and add $^1/_4$ its vol. of alc. After 24 hrs. filter the soln. and wash the ppt. of $Na_2H_2Sb_2O_7$ at first with 40% alc. and gradually increase the proportion of alc. until at last a 75% alc. is used. Dissolve the ppt. on the filter, allowing the soln. to drain into the original vessel to the sides of which considerable ppt. will adhere, in a mixt. of HCl and tartaric acid. In this soln. the Sb can be detd. gravimetrically after pptn. with H_2S or by iodometric titration. Evap. the alc. filtrate in a porcelain dish until the alc. is removed. Dil. to 300 cc. and add, while stirring, just as many cc. of 50% NH_4NO_3 soln. as there were cc. of 20% NaOH used in the previous treatment. This causes tin to ppt. as metastannic acid. Boil until the odor of NH_3 is no longer perceptible, filter and wash with hot, dil. NH_4NO_3 soln. Ignite and weigh as SnO_2. Concentrate the filtrate and ppt. the As by treatment with magnesia mixt. On account of the large quantity of Na salts present, it is advizable to dissolve the ppt. of $MgNH_4AsO_4$ in HCl and reppt. by the addition of NH_4OH. In the test anlyses, from about 80 to 900 mg. of each element were present and the av. error was less than 0.5 mg. The results for As, the last element detd., were particularly good. W. T. H.

Reductions with zinc and cadmium in volumetric analysis. W. D. TREADWELL, M. LÜTHY AND A. R. RHEINER. *Helvetica Chim. Acta* **4**, 551–65(1921).—The reduction of Fe^{+++} in a Jones reductor was studied although the Zn was not amalgamated as is customary in American practice. The reduction was found to take place best with solns. of low acidity and with Zn of fine grains. The results obtained were slightly above the theoretical value but no blank was run or correction applied to the titration. Expts. were tried with metallic Cd which is not capable of reducing an appreciable quantity of Fe to the metallic condition even in solns. of low acidity. A suitable Cd powder was prepared by the electrolysis of $CdSO_4$ solns. acid with H_2SO_4 and using a current of 30 amp. per sq. dm. As soon as

H_2 began to be evolved it was necessary to add more $CdSO_4$ to the bath. With a layer of Cd of only 5 to 7 cm. in the reductor tube, it was possible to secure complete reduction of Fe in slightly acid solns. and there was much less evolution of H_2 than when unamalgamated Zn was used. The use of the Cd reductor proved satisfactory for the reduction of $Ti(SO_4)_2$ solns. Perfect results in the subsequent $KMnO_4$ titration were obtained when the H_2SO_4 content varied from 0.9 to 18.8 g. H_2SO_4 with 10 cc. of 1 to 10 $Ti(SO_4)_2$ soln. There was much less neutralization of the acid by the Cd than takes place when Zn is used. The reduction of a soln. contg. both Fe^{+++} and Ti^{++++} with Cd gave a soln. which could be titrated electrometrically for both Ti and for Fe. With MoO_4^{--} the reduction with a Zn reductor apparently showed about 0.2% more than the theoretical reduction to Mo^{+++} but with Cd the results are correspondingly low. With a Cd reductor an acid soln. of NH_4VO_3 was reduced to within 2% of the theoretical reduction to V^{++}. With UO_2SO_4 the results indicated a reduction to the uranous condition. W. T. HALL

The use of hypophosphorous acid in gravimetric analysis. I. The determination of silver and its separation from lead and other metals. L. MOSER AND TH. KITTL. *Z. anal. Chem.* **60**, 145–61(1921).—H_3PO_2 in the presence of H^+ or OH^- ions is capable of causing the deposition of H and all metals below H in the potential series, *e. g.*, Cu, Bi, As, Sb, Hg, Ag, Pd, Pt, Au. At ordinary temp. H_3PO_2 is a moderately strong, monobasic acid but its ionization decreases with rise of temp. above 55°. Soly. expts. with Ag gel as pptd. by H_3PO_2 showed that about 3 mg. were dissolved by 1 liter of $^1/_4$ molar H_3PO_2 soln. or 1 mg. of Ag by $^1/_4$ molar H_3PO_2 at 25° but the soly. was only about $^1/_2$ as great at 70°. The P present in a sample of commercial H_3PO_2 was found to be 4.96% as H_3PO_3 and the balance as H_3PO_2, no H_3PO_4 being detected. The chief product of the oxidation of H_3PO_2 by its reaction with Ag^+ is H_3PO_3 but an appreciable quantity of H_3PO_4 is formed at the same time. Mawrow and Mollow (*C. A.* **3**, 1131) succeeded in detg. Ag quantitatively by means of H_3PO_2 but found that the values were always a trifle high. They were unable to separate Ag from Pb with this reagent because they washed the Ag gel with alcohol which caused pptn. of $Pb(H_3PO_2)_2$. The cause of the high results is now found to be due to adsorption of a small quantity of PO_4^{---} by the ppt. Accurate results in the detn. of Ag even in the presence of Pb were obtained by the following procedure. The results were found comparable with those obtained by well known standard methods for detg. Ag. Heat the Ag^+ soln., which should not be over 0.05 *N* to avoid adsorption errors, on the water-bath and treat with at least twice th theoretical quantity of H_3PO_2 required for the reduction of Ag^+. Allow the beaker to remain on the bath until the ppt. settles well and the supernatant liquid is perfectly clear. This requires about 30 min. with 0.05 *N* solns. and longer with more dil. solns. Filter without allowing the soln. to cool and wash with hot water until a considerable quantity of the filtrate will not decolorize a small drop of 0.01 *N* $KMnO_4$ soln., showing that all of the H_3PO_2 and H_3PO_3 has been removed. Dry the filter and ignite the paper and ppt. separately. W. T. HALL

Rapid determination of mercury in ores. A. HEINZELMANN. *Chem. Ztg.* **45**, 657–8(1921).—Place from 1 to 3 g. of the ore in a hard glass test-tube about 17 cm. long and 17 mm. wide. With the aid of a glass stirring rod, mix the ore with an equal vol. of powdered CaO and cover with a layer of 3–5 mm. of CaO. If the ore contains free S or pyrite the CaO should be mixed with Fe filings or with CuO. On top of this place a layer of asbestos pressed down with the glass rod so that its depth is about 3 mm. Tap the tube to make a narrow channel on top and suspend it in a nearly horizontal position by means of a clamp. Heat the contents of the tube very carefully with a small flame for 2 or 3 min. and then for 10 min. with a stronger flame. If considerable S is present, it is well to heat the upper layer contg. the Fe or CuO first in order to aid

the retention of the S. Soon after the beginning of the heating a slight gray sublimate will form about 3 cm. above the asbestos; the quantity of ore taken should not be sufficient to form drops of Hg. After the heating is finished draw out the end of the test-tube contg. the ore and flux and seal with a small blast flame so that a new tube is formed. Dissolve the Hg in 2 or 3 cc. of concd. HNO_3, placing the tube in hot water to aid the reaction. When no more nitrous fumes are evolved, dil. with 5 cc. of water and transfer the soln. to a 100 cc. Erlenmeyer flask, rinsing out the tube with 3 portions of 3 cc. of water. Add a few drops of 0.1 *N* $KMnO_4$ soln. to oxidize any Hg_2^{++} to Hg^{++}. Remove the excess $KMnO_4$ by adding a little Fe^{++} soln. and add Na_2CO_3 until HgO begins to ppt. Dissolve this in dil. HNO_3, add ferric alum indicator soln. and titrate with CNS^- soln. by the Volhard method. Expts. with $HgCl_2$ mixed with 2 g. CaO showed that over 98% of the Hg was recovered by this simple method and in the analysis of ores contg. 1 to 4% Hg the results were excellent. W. T. HALL

The electro-analytical separation of mercury and copper. W. BÖTTGER. *Z. angew. Chem.* **34**, Aufsatzteil, 120–2(1921); cf. *C. A.* **15**, 482.—The electrolytic sepn. of Hg and Cu is not difficult when both metals are present as nitrates. If chloride is present, however, the e. m. f. must be raised on account of the slight ionization of $HgCl_2$ and there is danger of Cu being pptd. The simplest way to overcome this difficulty is to ppt. the 2 metals together and, after dissolving the weighed deposit in HNO_3, deposit the Hg and Ag (from the Ag-plated cathode which should be used to prevent loss of Pt) in the usual way. The directions are as follows: To about 80 cc. of the neutral soln. contg. chloride, add 4 cc. of concd. HNO_3 and 3 cc. of alc. Electrolyze with a current at 2.2 volts potential. The current of 3 amp. soon weakens to about 1.5 amp. and chiefly Hg is deposited. Raise the potential then to 2.4 volts and a current of about 2.6 amp. will flow. In the stirred electrolyte, the current will fall to about 80 milliamp. in 10–15 min., when all the Cu and Hg is deposited. Dissolve the weighed deposit in 3 *N* HNO_3, neutralize with NH_4OH, add HNO_3 and alcohol and deposit Ag and Hg with a current at 1.4 volts. In the sepn. of Hg and Cu in a KCN bath the directions given by E. F. Smith and C. R. Spare do not agree with those of Goecke. Students working under B. have confirmed the data given by Goecke but an explanation of the results obtained by Smith show that both observers were probably correct but worked under different conditions. The soln. of the 2 metals treated with 5 cc. of concd. NH_4OH for 0.5 g. of metal can be electrolyzed with a current of 3 amp. at 2.9 volts, or with a little less. As the current weakens the voltage is raised up to 3 volts. For the usual quantities of metal, all the Hg is deposited in about 20 min. The addition of the NH_4OH *before* the KCN is important. Otherwise a clear soln. is not obtained and there is considerable decompn. of cyanide during the electrolysis. The deposition of Cu from a soln. treated as above with NH_4OH and KCN takes place at room temp. with an e. m. f. of 3.20 volts but if the NH_4OH was not added from 3.80 to 4.50 volts are required. At 65° the decompn. potential is about 2 volts or less. W. T. H.

The separation of tin and antimony in hydrochloric acid solution by hydrogen sulfide. G. LUFF. *Chem. Ztg.* **45**, 229–31, 254–5, 274(1921).—The results of 40 expts. are recorded, most of which gave good results, which shows that if the directions are followed closely good results may be obtained by the methods of Vortmann-Metzel, of Panajotow-Prim, or of Clarke-Henz. Preliminary expts. showed, however, that it is advantageous to ppt. the Sb in the presence of 16.5 g. of NH_4Cl. If this salt is present it is possible to ppt. Sb as sulfide in the presence of Sn^{++++} with from 8 to 30 cc. of concd. HCl present per 100 cc. of soln. It is well to work with 14 cc. concd. HCl per 100 cc. of soln. The sepn. succeeds when the Sb is tervalent or quinquevalent and the Sn is quadrivalent. To the original acid soln. add NH_4OH until a yellow color is obtained with methyl orange indicator. Add NH_4Cl to make a total of 16.5 g. and 42 cc. of concd. HCl.

Dil. to 300 cc. and weigh the flask and its contents, including a gas delivery tube and thermometer, on a rough balance. Heat on a sand bath to about 100° and introduce a rapid stream of H_2S for $^3/_4$ hr. Add hot water until the original wt. of the flask is obtained and introduce H_2S for 5 minutes longer. Allow to cool to 30° and filter off the Sb sulfide ppt. The above procedure was used for the sepn. of quinquevalent Sb from quadrivalent Sn. When the Sb was tervalent, the procedure was the same except that the soln. was at first dild. to only 250 cc., 35 cc. of concd. HCl were added and the soln. was allowed to cool while the H_2S was being introduced. The pptn. was started at 98°. After $^1/_2$ hr. the temp. was raised to 90°, the soln. brought to its original vol. with hot water and treated with H_2S for 5 minutes longer before cooling to 30°. The procedure will take care of 0.25 g. of Sb and probably an equal quantity of Sn. The Sb values were obtained by titration with I_2 in $NaHCO_3$ soln. after reduction, if necessary, by treatment with KI in acid soln. and also by weighing as Sb_2S_3 after heating in CO_2. The Sn values were obtained for the most part by the method of Löwenthal. W. T. H.

The electrolytic determination of gold and its separation from copper, palladium and platinum. W. D. Treadwell. *Helvetica Chim. Acta* 4, 364–74(1921).—A KCN bath, although most suitable for the deposition of Au, does not lend itself well to sepns. of Au from elements such as Cu, Pt and Pd. For this reason expts. were made with chloride solns. To 120 cc. of nearly neutral soln. 1 or 2 cc. of concd. HCl was added, then 1 or 2 g. of NH_4OAc and the soln. was electrolyzed with a gauze cathode and spiral anode. The electrolysis was started in the cold with 1.0–1.3 volt corresponding to a current of 0.1–0.15 amp. The soln. was heated slowly to 50° or 60° and stirred with a slow stream of N_2 or CO_2. Toward the last the current weakened rapidly. Excellent results were obtained and the effect of considerable Cu was not noticeable. *Separation of gold from palladium.*—To deposit Au in the presence of Pd it is necessary to keep the e. m. f. considerably below 1 volt. Good results were obtained by the electrolysis of HCl solns. in the presence of NH_4OAc when the e. m. f. was 0.4–0.5 volt. 2 coaxial gauze electrodes were used 3 mm. apart. After the Au was deposited, the cathode was changed and the Pd deposited by raising the e. m. f. to about 1.2 volt. *Separation of gold from platinum.*—In this case also the separation was accomplished in a bath contg. 2 cc. of concd. HCl and 2 or 3 g. of acetate. The Au was deposited at 0.5–0.7 volt and the Pt at 1.5 volts. A Pt dish served as cathode and a rotating disk as anode. During the electrolysis the temp. was raised gradually to about 60°. Under similar conditions a sepn. of Au from both Pd and Pt was effected. Owing to the greater soly. of Pd it was found possible to place a ppt. of these 2 metals contg. 0.387 g. Pd and 0.0170 g. Pt in a bath of 0.5 cc. HCl and 3 g. NaOAc in about 120 cc. of H_2O and obtain all the Pd on the cathode after electrolysis for 1 hr. at 1–1.5 volts. W. T. H.

Quantitative determination of potash by the spectrum. D. Paul Rogers. *Chem. Met. Eng.* **25**, 161(1921).—For the detn. of water-sol. K, boil 10 g. of a sample such as flue dust with 30 cc. of water for 30 min. Filter and concentrate to 10 cc. Make a loop in the end of a Pt wire by wrapping it around the lead of a pencil. Dip the loop in the soln. and then into the flame, viewing it with blue spectacles against a white background in a dark room and det. the time in sec. that the K flame persists. 0.5 sec. was found equivalent to about 0.25 g. K_2O in 10 cc. of soln. The av. of about 20 readings gives a value which approximates the truth as detd. by a standard method. W. T. H.

New method for the determination of potassium. St. Minovici and C. Kollo. *Bul. soc. chim. Romînia* 3, 17–25(1921).—This method depends upon the pptn. of K as $KHC_4H_4O_6$ but, unlike similar methods which have been described, it does not depend upon the use of alc. to decrease the soly. of the $KHC_4H_4O_6$ and the presence of Na or acids such as sulfate or phosphate does no harm. Preliminary expts. showed that the

soly. of $KHC_4H_4O_6$ in a satd. soln. of $NaHC_4H_4O_6$, or in the presence of excess $H_2C_4H_4O_6$ soln. which had been satd. with the K salt, is inappreciable. Thus although pure water at 20° dissolves 0.57% of its wt. of $KHC_4H_4O_6$, only 0.01% dissolves in a 7.5% soln. of $NaHC_4H_4O_6$ and less in a satd. soln. For the analysis, dissolve 0.25–0.3 g. of the salt in 5 cc. of water, add 0.5–0.6 g. of powdered $NaHC_4H_4O_6$ and allow the mixt. to stand 1 hr. with occasional stirring. Add 5 cc. of 5% $H_2C_4H_4O_6$ soln. (which has previously been allowed to stand in contact for 5 or 6 days with 1 g. $KHC_4H_4O_6$ for each 100 cc. of soln.) and filter. Wash twice more by decantation with 5 cc. portions of the tartaric acid; this serves to dissolve the excess of $NaHC_4H_4O_6$. Then wash on the filter with 50 cc. of a mixt. of equal parts alc. and ether to dissolve the excess tartaric acid. The ppt. may be weighed upon a tared filter or, as is recommended, it may be dissolved in boiling water and titrated with standard NaOH soln. using phenolphthalein as indicator. To the wt. of K_2O found 0.005 g. should be added to allow for the slight soly. of $KHC_4H_4O_6$. The results reported agree satisfactorily. W. T. H.

The characterization and determination of potassium as picrate. ST. MINOVICI AND AL. IONESCU. *Bul. soc. chim. România* **3**, 25–33(1921).—In place of a satd. soln. of Na picrate, which has been recommended by Reichard, a satd. soln. of picric acid in ethyl malonate is very efficient for the microscopic detection of K. One drop of a 0.1% soln. will give a characteristic ppt. even in the presence of Na and K. The reagent is too expensive and too slightly sol. in water for use in the quantitative detn. of K. Fortunately a satd. soln. of picric acid in 95% alc. is even more efficient as a precipitant. It permits the pptn. of as little as 0.01 mg. of K salt. When this reagent is used alone there is danger, particularly on evapn., of some Na or NH_4 salt being pptd. but this difficulty can be overcome by the addition of 5% of glycerol. With this reagent it is possible to detect less than 0.01 mg. of K under the microscope. It may be used also for the quant. detn. of K as follows: To 10 cc. of soln. contg. 1 g. of K salt, add 20 cc. of the alc.-glycerol soln. of picric acid and allow to stand 5 min. with frequent stirring. Filter through a double filter which has been previously weighed. Wash the ppt. with 20 cc. of ether to dissolve any picric acid and dry 24 hr. in desiccator contg. $CaCl_2$. The computation made on a basis of 39 g. K to 267 g. picrate shows that the results are about 0.015% too low. Excellent results were obtained in the analysis of the chloride, bromide, iodide, chlorate, sulfate, bisulfate, dichormate, nitrate, phosphate, bicarbonate, carbonate, ferrocyanide, acetate, oxalate of K and of Rochelle salt. The procedure is unaffected by the presence of 1% or less of either Na or NH_4. Instead of weighing the ppt. it can be titrated as follows: Dissolve the ppt. in 100 cc. of water and add from a buret a soln. of quinine acid sulfate, which causes the pptn. of picric acid. The end of the pptn. is reached when a small quantity of the filtered soln. will give no further pptn. with 1 drop of quinine soln. The end-point is also indicated by the fact that the supernatant soln. is nearly colorless when all the picric acid is pptd. The pptn. takes place according to the following equation: $C_{20}H_{24}N_2O_2.3H_2O + 2C_6H_2(NO_2)_3OK + H_2SO_4 = C_{20}H_{24}N_2O_2.[C_6H_2(NO_2)_3OH]_2 + K_2SO_4 + 3H_2O$. According to this equation, 324 g. of quinine is equivalent to 534 g. of K picrate, or to 78 g. of K. The quinine soln. should contain about 2% of the alkaloid with 2 cc. of sulfuric acid per 100 cc. The titer of the soln. may be obtained by detg. how much is used in the analysis of a known quantity of K salt or by the titration of a soln. contg. a known quantity of picric acid. W. T. H.

New method for the separation of the alkaline-earth metals and their quantitative determination. VIRGINIE THEODOSSIU. *Bul. soc. chim. România* **3**, 34–40(1921).—Ba, Sr and Ca are first pptd. as sulfates and the ppt. boiled with NH_4 citrate soln. which causes Ca to dissolve as citrate. The residue of $BaSO_4$ and $CaSO_4$ is warmed with $(NH_4)_2CO_3$ soln., which transforms $SrSO_4$ into $SrCO_3$ and has no effect upon $BaSO_4$.

The $SrCO_3$ is dissolved by dil. acid. The NH_4 citrate soln. is prepared as follows: Dissolve 42 g. of citric acid in 200 cc. of water, neutralize with NH_4OH and dil. to 1000. This gives a 0.2 molal soln. A crystal of thymol, or a few drops of $CHCl_3$ should be added as preservative. The details of analysis are as follows: To the hot soln. of 0.5–0.6 g. of the chlorides or nitrates add sufficient H_2SO_4, dild. with twice its vol. of water, to form the sulfates of the 3 alkaline earths. Heat on the water-bath until the sulfates of Ba and Sr have settled out, allow to cool and add 2 vols. of 90% alc. Stir well and allow to stand 4 hrs. Decant the soln. through a filter, disturbing the ppt. as little as possible. To the ppt. add a few drops of NH_4OH to neutralize the excess H_2SO_4 and treat with 10 cc. of NH_4 citrate soln. for each 0.1 g. of $CaSO_4$ present, adding the reagent through the same filter. Digest for 3 hrs. with occasional stirring. Filter the soln. again through the same filter and wash water until no more Ca passes into the filtrate. Det. the Ca as oxalate according to the standard gravimetric or volumetric method. Ignite and weigh the ppt. of $SrSO_4$ and $BaSO_4$. To the contents of the crucible add 20% $(NH_4)_2CO_3$ soln. and digest at the boiling temp. for 15 min. In this way $SrCO_3$ is formed. Add HCl to acid reaction, dil. with water and again heat to boiling. Filter and repeat the treatment until a trace of the residue will no longer give the crimson Sr test in the flame. Collect all of the ppt. on a filter, ignite and weigh the $BaSO_4$. Det. the Sr by difference. The results expressed in terms of CaO, SrO and BaO average within less than a 1 mg. of the truth and the method was found much more satisfactory than the classic method of Rose-Strohmeyer-Fresenius. W. T. H.

Determination of bismuth. O. A. Critchett. *Eng. Mining J.* **112**, 58(1921).—Dissolve 0.5–1 g. of ore in HCl and HNO_3 and evap. to fumes with 20 cc. of 50% H_2SO_4 by vol. Cool, dil. to 75 cc., add a drop of HCl to ppt. Ag and filter, washing with 10% H_2SO_4 by vol. To the filtrate add Al foil and 10 cc. of $Na_2S_2O_3$ soln. Boil 20 min. and filter. If the Al is clean remove it; otherwise keep it in the beaker. Wash back the ppt. into this beaker, using hot water, and add 2 or 3 g. of solid KOH. Remove the Al foil and wash it. Boil the liquid in the beaker for 10 min. to dissolve excess of S and any As, Sb or Sn. Filter through the same paper as was used before. Place the filter and ppt. back in the beaker, add 10 cc. HNO_3 and 6 cc. H_2SO_4. Evap. to fumes or until the soln. turns black owing to the charring of the paper. Add 5 cc. more of HNO_3 and evap. again, repeating this treatment until all the paper is destroyed and no blackness results on evapg. Dil. to 50 cc., heat to boiling and filter, washing with a little 10% H_2SO_4. Heat the filtrate, make it slightly ammoniacal, boil and filter, washing with hot water. Dissolve the ppt. on the paper with 5 cc. of HNO_3 and 20 cc. of boiling-hot water, catching the filtrate in a clean beaker. Det. the Bi as oxide after treatment with $(NH_4)_2CO_3$, as BiOCl after neutralizing with NH_4OH, adding a little HCl, dilg. and boiling, or by $KMnO_4$ titration as follows: Dil. the $Bi(NO_3)_3$ soln. to about 150 cc., add 5 g. $(NH_4)_2C_2O_4$ and boil 5 min. Filter and wash the $Bi_2(C_2O_4)_3$ ppt. by decantation with hot water. Dissolve in acid and titrate with $KMnO_4$. W. T. H.

Estimation of bismuth in high grade ores. G. Spurge. *Chem. Age* (London) **4**, 584(1921).—The method depends upon a comparison of the color produced with KI in dil. HNO_3 soln. with that obtained similarly with a soln. contg. a known quantity of Bi. Dissolve 0.05 g. of the powdered ore, if the sample contains 3% Bi or more, in 25 cc. of HNO_3 and 75 cc. of water. Boil 10 min., cool and dil. to 500 cc. in a calibrated flask. Transfer a part of the mixed soln. to a buret and det. how much is required to give with KI a color comparable with that produced with 1 cc. (0.05 g. Bi) of a standard Bi soln. which has been treated with 10 cc. of 10% KI soln., 3 drops of H_2SO_3 and dild. up to the mark of a 50 cc. Nessler tube. The presence of Cu does not seem to interfere with the test if the color comparison is made immediately but Pb should be removed as sulfate. W. T. Hall.

Notes on gravimetric methods of analysis. XVII. L. W. WINKLER. *Z. angew. Chem.* **34**, Aufsatzteil, 235–6(1921).—The directions recommended for the *pptn. of Zn* as $ZnNH_4PO_4$ are similar to those of Dakin and others except that, for some unmentioned reason, the pptn. is made in slightly ammoniacal soln. Most of the values obtained were a little low. The results obtained by weighing the ppt. after drying at 130° were somewhat better than those obtained after ignition to $Zn_2P_2O_7$. If KCl is present in the soln. contg. Zn, the ppt. tends to run through a cotton wool filter and some of the NH_4 in the ppt. is likely to be replaced by K. W. T. HALL

The determination of zinc as zinc ammonium phosphate. G. LUFF. *Chem.-Ztg.* **45**, 613–4(1921).—The weak points of the method have been studied in detail, and, in spite of the slight soly. of $ZnNH_4PO_4$ in water, in NH_4Cl solns. and in $NH_4H_2PO_4$ soln., accurate results are obtained if an excess of $(NH_4)_2HPO_4$ is used and care is taken to keep the soln. practically neutral. W. T. HALL

Volumetric determination of zinc. I. M. KOLTHOFF AND J. C. VAN DIJK. Utrecht. *Pharm. Weekblad* **58**, 538–53(1921).—Both the direct and indirect acidimetric methods of detg. Zn are accurate within about 1% if properly carried out. They are not specific and are applicable in general only to pure Zn salts. The KCN method is less satisfactory than the $K_2Hg(CNS)_4$ method. The latter gives excellent results in absence of Cl^-; SO_4^{--} and NO_3^- do not interfere. When the Zn^{++} concn. is above 0.01 *N* the soln. may be filtered immediately after adding the reagent; if less than 0.01 *N*, the soln. should stand 1 day before filtering. The excess of reagent in the filtrate, to be titrated back by the Volhard method, must be not less than 0.06 *N*.

JULIAN F. SMITH

Determination of zinc by the ferrocyanide method. C. E. BARRS. *J. Soc. Chem. Ind.* **40**, 168T(1921).—When evapg. the soln. of an ore to dryness overheating may cause some of the Mn to dissolve in the method of Olivier (*C. A.* **15**, 2807). It is better to use $K_2C_4H_4O_6$ than $KHC_4H_4O_6$ on account of the greater soly. of the neutral salt. W. T. H.

The volumetric determination of aluminium in its salts. Correction. ALFRED TINGLE. *J. Ind. Eng. Chem.* **13**, 655(1921).—Typographical errors in the paper recently published (cf. *C. A.* **15** 2801) are corrected. W. T. H.

A method for the rough analysis of iron and manganese in systematic qualitative analysis. L. J. CURTMAN AND N. H. HECHT. *Chem. News* **122**, 254–5(1921).—Treat the ppt. produced by NH_4OH and $(NH_4)_2S$ in the usual qual. scheme of analysis with 60–80 cc. of HCl (1:9) and filter off the undissolved NiS and CoS. Evap. to 2 cc., transfer to a 50 cc. graduate and dil. to 50 cc. with water. *Detn. of Fe.*—Treat 25 cc. of the soln. with 10 cc. of 6 *N* NaOH and 1.5 g. of Na_2O_2. Boil for a few min. to decomp. the excess peroxide, dil. with an equal vol. of water and filter. Dissolve the washed ppt. in 50 cc. of concd. HCl, dil. and filter off any paper. In an open Erlenmeyer flask boil down the soln. to half its original vol., cool to room temp. and titrate with standard $SnCl_2$ soln. using KCNS as indicator. *Detn. of Mn.*—To the other 25 cc. of HCl soln. in the graduate, add NaOH and Na_2O_2 as before but wash the resulting ppt. carefully until all chloride is removed. In a beaker, treat the ppt. and filter with a mixt. of 25 cc. concd. HNO_3 and 10 cc. of 3% H_2O_2. When the ppt. is all dissolved, boil down to half the original vol. in an Erlenmeyer flask. Cool, transfer to a 100 cc. graduate and dil. to 100 cc. with water. Mix and take 20 cc. for the Mn detn. Neutralize with NH_4OH, add 10 cc. of concd. HNO_3 and dil. to 200 cc. Add 4 g. of $NaBiO_3$, stir and after 5 or 10 min. filter through a fluted paper. Wash the ppt. with 5% HNO_3 and titrate the filtrate with 0.3% H_2O_2. W. T. HALL

The estimation of small amounts of chromium in steels. B. S. EVANS. *Analyst* **46**, 285(1921).—Since the publication of a former paper (*C. A.* **15**, 1264) E.'s attention has

been called to the sensitive color reaction of chromic acid and diphenylsemicarbazide (cf. Cazeneuve *Analyst* **25**, 331(1900)). An intense purple color is produced similar to that of permanganate. Small quantities of 0.01 *N* $K_2Cr_2O_7$ soln. were added to solns. contg. 4 g. of dissolved electrolytic Fe and the colors produced compared with that obtained with similar solns. contg. no Fe. The Cr content in the expts. corresponded to from 0.004 to 0.0017% and the results obtained were accurate to about 0.0001%. To prepare the reagent dissolve 1 g. of diphenylsemicarbazide in 10 cc. AcOH and dil. to 1000 cc. with water. In making the color test add 5 cc. of this reagent and 10 cc. of 25% H_2SO_4 by vol. W. T. HALL

A study of methods for the determination of total carbon and a new method for determining graphitic carbon in ferrous alloys. P. WENGER AND A. TRAMPLER. *Helvetica Chim. Acta* **4**, 547–51(1921).—The results obtained in the analysis of alloys contg. a high content of metal other than Fe, *e. g.*, Fe-Mo, Fe-Si, Fe-Mn, Fe-Cr and Fe-V, with C varying from 0.2 to 8.3% may be summarized as follows: (1) Combustion in an elec. furnace is more satisfactory than wet combustion by the method of Corleis. The results are more consistent and they are obtained more quickly. All sorts of Fe alloys may be analyzed in this way without preliminary chem. treatment. (2) The graphitic C in Fe-Mn, Fe-V, Fe-Cr and Fe-Si may be obtained by dissolving the metal in H_3PO_4. Heat 100 cc. of the acid in a Pt dish to at least 150°, and add 1 g. of the finely pulverized alloy in small portions. The temp. off the acid should not be raised above 250° although Fe-Si is not attacked below 230°. The addition of HF is favorable with Fe-Si but the addition of HCl, HNO_3 or H_2SO_4 is unfavorable. There is usually a residue of unattached metal after this treatment. Decant off the soln. and replace with 25 cc. of fresh H_3PO_4 and again heat. Filter without dilg. through a Gooch crucible contg. asbestos, dry and ignite in the elec. furnace. W. T. HALL

Analysis of tungsten. GASTONE FIORENTINO. *Giorn. chim. ind. applicata* **3**, 56–8(1921).—*Volumetric detn. of tungstic acid.* To the soln. of an alkali tungstate (containing no excess of alkali salts), add 8 cc. concd. NH_4OH. For hydrated tungstic acid, such as is generally obtained in analysis, add 25 cc. H_2O and 8–10 cc. strong NH_4OH, and heat gently until all the tungstic acid is dissolved. Make the liquid up to about 200 cc.; and acidify slightly to litmus paper with AcOH. Neutralize exactly with NH_4OH so that the litmus is rather towards the blue and there is an excess of 1 or 2 drops of NH_4OH. Boil for a few minutes until the litmus paper has turned to a wine red. To the boiling soln. add from a buret a measured excess of titrated, slightly acid Pb acetate, mixing continually. Boil anew until the ppt. at first flocculent and voluminous becomes cryst. Then det. in the soln., without filtering, the excess of Pb by means of a titrated aq. soln. of NH_4 molybdate. The molybdate is added until a drop of the liquid does not give a yellow coloration when placed in contact with a drop of a freshly prepd. soln. of 0.10 g. pure tannin in 10 cc. H_2O. Make a blank test upon 200 cc. H_2O. In case an excess of molybdate soln. is used, add again a measured excess of Pb acetate, and retitrate with the molybdate. *Volumetric detn. of tungstic acid in minerals and concentrates.*—Heat for 1 hr. at 60° 1.5 g. mineral (finely powdered in an agate mortar) with 100 cc. concd. HCl. Then evap. to $^1/_2$ its vol., add 20 cc. HNO_3, and evap. again to 25 cc. Add 5 cc. more HNO_3, and evap. to 15–20 cc. Add 180 cc. boiling H_2O, stir well and allow to stand for some hrs. Filter and wash by decantation with 1% HNO_3. For rapid work where great exactness is not required, place the filter in the beaker contg. the greater part of the ppt. Add 8–10 cc. NH_4OH and 25 cc. H_2O; heat gently for some minutes until all the tungstic acid is dissolved. Observe if the mineral has been completely attacked. The residue should show no undecomposed black specks of mineral. If the mineral or concentrate is rather poor, transfer the liquid to another high-form 350-cc. beaker, washing the first beaker and the filter, which may be left

entire, with H_2O until the vol. in the second beaker is about 200 cc. Det. tungstic acid as before described. For rich minerals or concentrates take an aliquot part contg. about 0.25 g. WO_3. Add the proportional part of NH_4OH and dil. to 200 cc. with H_2O. Proceed as before. For very exact detns., where possibly unattacked particles of mineral may be present (because very impure or not sufficiently pulverized), allow the filter to remain upon the funnel, pour over it a mixt. of 8 cc. NH_4OH and 25 cc. H_2O, receiving the liquid in the beaker containing the major portion of the ppt. Cover the beaker, warm gently for a few min. until the WO_3 is dissolved, filter upon the same filter into another beaker, wash with slightly ammoniacal H_2O and bring all the residue upon the filter. Proceed as before. Dry and ignite the filter contg. the residue at a moderate temp. in a porcelain crucible. Det. its content in WO_3 by the cinchonine method described below. Add this value to the quantity obtained volumetrically. For very exact analyses it is necessary to conc. the acid liquid from the first attack and the washing, and ppt. with cinchonine. *Gravimetric method of detg. tungstic acid with cinchonine.*—Fuse 8–10 g. pure NaOH in a small Fe crucible, adding traces of charcoal. Cool, add 0.5–1 g. of the mineral and a trace of charcoal, cover with an Fe lid and heat, gently at first, then to dull redness for 8–10 min. Pour the fused mass into a clean dry Fe or Ni dish floating upon H_2O in another dish or beaker. Place the crucible in a porcelain dish contg. a little H_2O and warm lightly until the residue adhering to the crucible is dissolved. Remove and wash the crucible and the lid. Allow the washings to fall into the dish. Into this bring the fusion contained in the metal dish. Dissolve the whole by boiling, and add 4–5 g. solid $(NH_4)_2CO_3$ to diminish the alkalinity of the soda, which otherwise would tear the filter. Boil for a few min. longer, filter and wash with H_2O made slightly alk. with NaOH, receiving the filtrate and washings into a beaker. Cover, warm, and pour therein, little by little, 30 cc. concd. HCl. Boil for a few min., remove from the heat and add 8–10 cc. concd. soln. of cinchonine (prepd. by dissolving 30 g. cinchonine in 50 cc. concd. HCl and 250 cc. H_2O), mix well and allow to stand for some hrs. Filter, wash at first 3–4 times with a dil. soln. of cinchonine (30 g. of the concd. soln. + 30 cc. HCl + 1000 cc. H_2O) and finally once with cold H_2O. (In the filtrate det. Sn by the Pearce-Low method.) Digest the filter and contents with 8–10 cc. NH_4OH and 25 cc. H_2O, warm gently for a few min., filter and wash with H_2O containing a little NH_4OH. Expel the excess of NH_4OH from the filtrate by heating. Then at once, while stirring, add 2–3 drops HCl and then at one time 8–10 cc. concd. cinchonine soln., mixing well for some min. Allow to stand for 1–2 hrs., filter through a filter contg. a little filter paper pulp, wash as above with dil. cinchonine soln., and then once with cold H_2O, dry, and ignite carefully in a Pt dish. Allow to cool and reheat strongly several times to assure of the burning of all the C contained in the ppt.; weigh as WO_3. For exact analysis, add 1–2 drops dil. H_2SO_4 and a little HF, evap., add 1–2 drops HNO_3, drive out the HNO_3 and H_2SO_4, ignite and weigh. The SiO_2 content is generally small. The cinchonine, which is costly, may be recovered from the liquids containing it by rendering them alk. with NH_4OH. R. S. P.

A method of determining nickel in Silverhorn ores. E. C. D. Marriage. *Eng. Mining J.* **112,** 174(1921).—The method consists in dissolving the ore in HNO_3 and $KClO_3$, removing SiO_2, pptg. Mn by treatment with Br and NH_4OH, removing elements of the first 2 groups by means of H_2S and titrating the Ni by the cyanide method in the presence of NH_4 citrate. W. T. H.

Notes on some technical methods of analysis. A. Whitby and J. P. Beardwood. *J. Chem. Met. Soc. S. Africa* **21,** 198–9(1921).—In the *detn. of Ni and Co in ores* by the method recommended by Low, there is some danger that $FeAsO_4$ will be dissolved by the excess of NH_4OH. The As may be removed by pouring the soln., obtained by dissolving an ore in *aqua regia* and adding citric acid, into NaOH and Na_2S; the Ni

and Co will be pptd. as sulfides with other metals but the As will remain dissolved as thioarsenate. In the *detn. of Cr in chromite*, the residue insol. in water, obtained by fusion of the sample with Na_2O_2, sometimes contains Cr. This can be removed by washing with Na_2O_2 soln. W. T. HALL.

Notes on some reactions of xanthates. A. WHITBY AND J. P. BEARDWOOD. *J. Chem. Met. Soc. S. Africa* **21**, 199–200(1921).—The alkali salts of xanthic acid are sol. in water but most of the other xanthates are insol. The Ni salt is easily dissolved by NH_4OH but the Co and Cu salts are not. On the basis of this fact a sepn. of Ni from Co and Cu has been worked out. *Sepn. of Ni and Co.*—To a soln. contg. dissolved salts of these metals, add 1 g. of citric acid and NH_4OH in excess. Add 1 g. of alkali xanthate and acetic acid to ppt. the xanthates of Ni and Co. After allowing to stand 3 hrs. at a temp. somewhat below the b. p., filter and wash with hot water. Transfer the ppt. back to the beaker and treat with approx. 8 *N* NH_4OH. Heat on the water bath, filter and wash with dil. NH_4OH until the filtrate shows no trace of yellow color. The Ni is now in the filtrate and the Co on the filter. The xanthate of Ni can be pptd. by adding AcOH. Upon ignition to a full red heat in a muffle with free access of air, the ppts. are changed to Co_3O_4 and NiO, respectively, in which forms they may be weighed. If Cu is present it behaves like Co but is weighed as CuO. From the mixt. of CuO and Co_3O_4 the Cu can be obtained by dissolving the oxides and pptg. with H_2S. The presence of ferric Fe or of As does not interfere with this procedure. W. T. H.

Notes on routine assaying at the Globe and Phoenix mine, Southern Rhodesia. H. R. EDWARDS. *J. Chem. Met. Mining Soc. S. Africa* **21**, 45–50(1921).—A former paper (*C. A.* **14**, 2770) was confined mostly to the physical side of assaying. The present paper is an amplification and a reply to the discussion provoked by the reading of the original paper. The points discussed are: sampling of ores, crushers, construction of the furnace, size of furnace, fluxes, cupels, cupel plates, soln. assays, air pressure filters, the effect of impurities on soln. assays made by Cu methods and the effect of HCl and H_2SO_4 when used with Cu_2Cl_2 in assaying plant solns. contg. thiocyanates, ferrocyanides and other impurities. W. T. H.

The behavior of sodium sulfantimonate (Schlippe's salt) toward solutions of certain salts. A. LANGHANS. *Z. anal. Chem.* **60**, 91–3(1921).—Sb sulfide forms complex sulfides with other metals such as are found, for example, in the minerals zinkenite, stephanite, and bournonite. For most of the expts. here described, a freshly prepared, 20% soln. was used of Na_3SbS_4 crystals, from which adhering Sb_2S_5 had been rinsed off, and tested with 5% solns. of various salts. The results obtained in this incompleted investigation are as follows: (1) *Alum:* treatment with an excess of Schlippe's salt gives a brownish red, flocculent ppt. with evolution of H_2S. (2) *Aluminium sulfate:* same as with 1. (3) *Chrome alum:* same as with 1. (4) *Zinc chloride:* lemon-yellow ppt. which turns orange-red on standing or upon being boiled. (5) *Manganous chloride:* orange ppt. which becomes darker on boiling and H_2S is evolved. (6) *Ferrous sulfate:* a black ppt. of FeS is formed immediately. (7) *Ferric chloride:* if an excess of the reagent is added, a black ppt. is formed which is unchanged by boiling. With the dilute reagent, a black ppt. is formed at first which soon becomes olive gray and on boiling the color changes to yellow. (8) *Silver nitrate:* if the reagent is present in excess, a reddish brown ppt. is formed but with an excess of silver a black ppt. results. (9) *Nickel sulfate:* a black precipitate. (10) *Cobalt sulfate:* same as with Ni but the test is not quite so sensitive. (11) *Cadmium acetate:* pure yellow ppt. becoming chocolate-brown on warming. (12) *Copper sulfate:* rust-brown ppt. unchanged upon heating. (13) *Bismuth nitrate:* brownish black ppt., odor of H_2S. (14) *Lead nitrate:* reddish brown ppt. (15) *Mercuric oxide:* a black ppt. The same result was obtained with mercuric oxalate and solns. of $Hg(NO_3)_2$ but with $HgBr_2$ a pure yellow ppt. was obtained.

(16) *Mercuric cyanide:* if the solid cyanide is covered with the reagent a yellow ppt. is obtained which gradually turns black without evolution of H_2S. In a soln. of the cyanide, a yellow ppt. is obtained; the ppt. turns black only when the antimonate is not present in excess. (17) *Solid mercury fulminate:* a yellow ppt. is formed on pouring the antimonate soln. over the solid; the ppt. after a short time turns green and finally black even when an excess of reagent has been added. (18) *Mercuric chloride:* a red ppt. is obtained with a little of the reagent which becomes lighter on shaking and finally pure white. If considerable reagent is added the ppt. is reddish yellow and brown on boiling. With 1% antimonate soln. an orange ppt. is obtained. (19) K_2HgI_4: an orange ppt. which turns olive brown on heating. (20) *Sodium stannate and arsenate* do not react with the antimonate. W. T. HALL

Determination of the volatile matter in graphite. OWEN L. SHINN. *J. Ind. Eng. Chem.* **13**, 633–4(1921). The volatile matter in graphite as detd. in coal analysis will give varying values according to the temp. and the time of heating. Good results are obtained by heating to 600° in N. Practically the same values can be obtained by heating the sample in a closed crucible for 30 sec. at 700°. W. T. H.

Modification of the Dumas method and the application of the Kjeldahl method to the determination of nitrogen in nitronaphthalenes. PAUL H. M.-P. BRINTON, F. M. SCHERTZ, W. G. CROCKETT AND P. P. MERKEL. *J. Ind. Eng. Chem.* **13**, 636–9(1921).—A modification of the Dumas method for the detn. of N in org. substances with high N content is described. NaOH is used in place of KOH in the nitrometer tubes, of which there are 3 used. A convenient app. for generating CO_2 by Na_2CO_3 soln. and H_2SO_4 is shown and precise manipulative details are given. The results obtained by the Kjeldahl-Gunning-Jodlbauer method are always low with this class of compounds but the variation increases as a linear function of the N content so that it is easy to plot a series of conversion factors; the modified Kjeldahl method may be used, therefore, in technical control and the proper correction easily applied. W. T. H.

The determination of sulfur dioxide in roaster gases according to A. Sander. B. C. STUER AND W. GROB. *Chem. Ztg.* **45**, 553–4(1921).—In a recent publication, A. Sander (*C. A.* **15**, 2805) has claimed that Hg causes catalytically some oxidation in mixts. of SO_2 and air. Doubting this, S. and G. have shaken SO_2 and air together with Hg and then titrated with I and with NaOH but found no evidence of oxidation. On the other hand, when SO_2 is conducted into NaOH there is likely to be some SO_4^{--} formed. Thus by passing the gas slowly and shaking with air, nearly 40% of the SO_2 was converted into SO_4^{--}. G. also claims priority for the method of detg. H_2SO_3, HSO_3^-, and SO_3^{--} alone and in the presence of SO_3^{--}. W. T. H.

The determination of sulfur dioxide in roaster gases. A. SANDER. *Chem. Ztg.* **45**, 554(1921).—In reply to criticism (cf. preceding abstr.), S. states that further expts. are being undertaken to det. the cause of the observed oxidation of SO_2. The method of sepn. referred to by Stuer and Grob was suggested by Walther Feld in 1898 but his explanation of the reaction as well as that suggested by Grob does not agree with that of S. W. T. H.

The determination of combustible gases in mine gases. LUDWIG WEIN. *Chem. Ztg.* **45**, 610–1(1921).—The content of the combustible gases, CO, CH_4 and H_2 is a measure of the condition of the air of a mine after a fire has taken place. In some cases as much as 7.6% of CO is present but usually not more than 3%. The content of this gas and similarly of CH_4 then diminishes rapidly, after the fire is quenched, and reaches proportions difficult to det. by ordinary means. A relatively simple app. is described in which the 3 gases, CO, CH_4 and H_2 can be detd. by one analysis. The CO is allowed to react with I_2O_5 and the liberated I titrated with $Na_2S_2O_3$, as is recommended when the CO content is low, or the resulting CO_2 is absorbed in a measured vol. of $Ba(OH)_2$ and

the excess detd. by titration. H_2 and CH_4 are oxidized by passing the gas over hot CuO. The CO_2 now formed is detd. by absorption in $Ba(OH)_2$ and titration of the excess. All of the water formed by the oxidation of the H_2 and CH_4 is weighed after absorption by $CaCl_2$ and deduction is made for that coming from the CH_4, so that the H_2 value is obtained. It is necessary to make sure that the gas is first freed from interfering substances such as CO, heavy hydrocarbons, C_2H_2, and C_2H_4. The gas to be analyzed is passed through a worm contg. Br_2 to react with unsatd. compds. and then through 4 wash bottles, 3 contg. 30% KOH and the fourth contg. concd. H_2SO_4. From the last wash bottle the gas passes through a tube contg. I_2O_5 which is heated to 110° by an oil bath. The I_2 evolved is collected in a small flask which is connected with a buret through which $Na_2S_2O_3$ can be added. The gas passes through this flask into 2 other flasks contg. a measured vol. of $Ba(OH)_2$ soln. The gas is then dried by H_2SO_4, granulated $CaCl_2$ and P_2O_5 and is passed through a combustion furnace with at least 25 cm. of CuO. The app. ends with a weighed $CaCl_2$ tube, 2 flasks contg. standard $Ba(OH)_2$ soln. and an aspirator. The gas should not be passed through the app. at a rate greater than 1 liter per hr. if it is rich in combustible gases, or faster than 2 liters per hr. if the content is low. The quantities of gas used in the expts. described varied from 100 cc. to 10 liters and the results obtained were excellent. W. T. H.

The determination of nitrogen in nitrates by the method of Arnd. O. Nolte. *Z. anal. Chem.* **60**, 167–8(1921).—This method which consists in reducing the NO_3^- in nearly neutral soln. to NH_3 by means of Cu and Mg and distg. the NH_3 into a measured vol. of standard acid, has been tested by Pilz who claimed that good results are obtained only under conditions quite different from those originally recommended. In this paper, the results obtained in the analysis of 25 samples by the method of Ulsch and by the original procedure of Arnd are compared. The agreement of values is remarkably good so that the Arnd method deserves to be called reliable in its original form. W. T. Hall

Sorption of water by certain powders as related to moisture determinations. K. Scheringa. Utrecht. *Pharm. Weekblad* **58**, 937–42(1921).—Some powders begin, at fairly high humidities, to take up small but weighable amts. of H_2O from air. Thus KBr begins at about 40% humidity, and from satd. air takes up about 7 mg. per 100 g. Pure ignited C, obtained by burning xylene, adsorbs about 7 mg. per 100 mg. Powdered KClO behaves much like KBr. Powdered sand, beginning a little above 10% humidity, takes up much larger amts. (more than 50 mg. per 100 g.); whereas powdered quartz takes up hardly any. Quartz, or good white sand, should therefore be used instead of ordinary sand in moisture detns. The water is not taken up, in these cases, by true adsorption or surface condensation. The real nature of the phenomenon is uncertain. Julian F. Smith

The electrometric titration of hypochlorous acid. W. D. Treadwell. *Helvetica Chim. Acta* **4**, 396–405(1921).—The available Cl of bleaching powder is usually detd. by titration but 2 difficulties are encountered. (1) Unless the conditions are right some chlorate is likely to be reduced and counted as hypochlorite or (2) some chlorate may be formed from hypochlorite during the analysis. It was found possible to avoid these difficulties by electrometric titration. As comparison electrode an 8 cm. long glass tube was taken, the end of which was drawn out into a capillary and turned upward. The end of the capillary was stoppered with filter paper or with a bit of gelatin contg. K_2SO_4. The tube was filled with K_2SO_4 soln. to which a little titrated hypochlorite soln. was added or a drop of very dil. KI_3 soln. As electrodes 2 bright Pt wires were used of which one was placed in the hypochlorite soln. and the other in the comparison electrode. The 2 electrodes were connected through a millivoltmeter with high resistance or through a galvanometer with suitable ballast resistance. The end-point

was shown by a sudden drop of the galvanometer to 0. Excellent results were obtained electrometrically by the Penot method of titrating the hypochlorite soln. with arsenite soln. contg. an excess of $NaHCO_3$ and by the Pontius method of titration in alkaline soln. with KI soln. W. T. H.

The estimation of hypochlorites and chlorates by hydrazine. ALEXANDER KILLEN MACBETH. *Chem. News* **122,** 268(1921).—Chlorites may be detd. gasometrically by by means of the following reaction: $2MClO + NH_2.NH_2 \longrightarrow 2MCl + 2H_2O + N_2$. Treat the alk. soln. in a Van Slyke nitrometer with 7 cc. of a hydrazine soln., obtained by dissolving 5–10 g. of hydrazine sulfate with 10–15 g. of KOH in 100 cc. of water. Very good results were obtained in the analysis of specially prepared alkali hypochlorite solns. and in the detn. of the available Cl in bleaching powder. The results agreed closely with those obtained by iodometric titration. An attempt to analyze chlorate similarly by the reaction suggested by G. Hodgkinson (*C. A.* **9,** 571). $2KClO_3 + 3[NH_2.NH_2.HNO_3] \rightarrow 6H_2O + 3N_2 + 3HNO_3 + 2KCl$, was unsuccessful. The reaction requires a catalyst but could not be made to take place quantitatively in the nitrometer. W. T. H.

An accurate method for determining the alkalinity in hypochlorite solutions. J. A. WESENER AND G. L. TELLER. *Am. J. Public Health* **11,** 613–6(1921).—The method depends upon the removal of active Cl by treatment with KI and Na_2SO_3 in the presence of HCl and titration of the excess of added acid by NaOH with methyl orange as indicator. The following reactions take place: $OCl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$; $I_2 + SO_3^{--} + H_2O \rightarrow SO_4^{--} + 2H^+ + 2I^-$. To 7 cc. of the hypochlorite soln. add 10 cc. of 10% KI soln. and 25 cc. of 0.1 *N* HCl. Add approx. 0.1 *N* $Na_2S_2O_3$ soln. from a buret until the yellow color due to I just disappears from the soln. Add 2 drops of 0.1% methyl orange soln. and titrate with 0.1 *N* NaOH. The method appears to be more accurate than that depending upon the removal of OCl^- by means of H_2O_2 or by evapg. with added NH_4OH. The test with dry phenolphthalein, which has been recommended, is shown to be unreliable. W. T. H.

A modification in the composition of iodine solution for the Reich test. H. M. LOWE. *J. Soc. Chem. Ind.* **40,** 123–4T(1921).—Standard I soln., used for testing gases for SO_2, may be made as follows: Dissolve 127 g. I in 30 g. NaOH with enough water to make 10 liters. The I reacts with the alkali to form iodate and iodide but on adding acid, all of the I is released. W. T. H.

The use of sodium persulfate in analysis. L. DÉBOURDEAUX. *Bull. sci. pharmacol.* **28,** 289–95(1921).—As in arsenical compds. can be detd. with accuracy as Ag_3AsO_4 when Na-persulfate is used to change the As to H_3AsO_4 and to decompose the carbonaceous matter of the org. material. A list of a dozen or more org. and inorg. As compds. is tabulated in which the As detn. by the methods previously outlined (cf. *C. A.* **15,** 2047, 2260), gives results that are fairly satisfactory. F. S. HAMMETT

The iodometric determination of arsenic acid. I. M. KOLTHOFF. Utrecht. *Pharm. Weekblad* **58,** 727–8(1921).—Contrary to the statements of Fleury (*C. A.* **14,** 2600), K. finds that atmospheric oxidation does not interfere with the iodometric titration of As_2O_5 as described by K. (*C. A.* **14,** 34). F.'s own method gives more accurate results than he claimed for it; a few min. heating on the water bath frees the titration flask from air so that the error from this source is negligible. J. F. S.

Argentometric determination of iodides. I. M. KOLTHOFF. Utrecht. *Pharm. Weekblad* **58,** 917–20(1921).—In the titration of I^- with $AgNO_3$ (*C. A.* **11,** 2868) the best protective colloid to hold the AgI in colloidal soln. is starch, since gum arabic takes up a small amt. of I. The method is applicable to very dil. solns. of I^- (0.0001 *N*). The interference of Cl^- and Br^- is about the same as in 0.1 *N* soln. Schneider's

method (*C. A.* 12, 1029) using $Pd(NO_3)_2$ as indicator is less accurate than when starch is used because the color change is less sharp. JULIAN F. SMITH

The determination of phosphoric acid as magnesium pyrophosphate. VI. D. BALAREFF. *Z. anorg. allgem. Chem.* **117**, 91–102(1921).—In a previous paper the work of Neubauer, Gooch and Austin, Järviner, Jörgensen, Schmitz and Bube was discussed (cf. *C. A.* **14**, 711) and in the light of B.'s experience certain apparent contradictions were explained. In the present paper the results obtained in the absence of MoO_4^{--} have been studied. The general conclusions drawn are as follows: (1) Methods which depend upon a single pptn. in the cold of $MgNH_4PO_4$ should be discarded for the results thus obtained are accurate only when the rate of pptn. and the quantities present of NH_4Cl, NH_3, alkali cations and SO_4^{--} anions vary only within narrow limits. (2) Methods depending upon a double pptn. give good results only when the first ppt. is dissolved in a fairly liberal quantity of HCl, when only Cl^- or NO_3^- anions are present and when the second pptn. is effected by the rapid addition of 10% NH_3 soln. (3) Jörgensen's method is inaccurate. (4) Järviner's method for detg. Mg gives too low values and when his method is applied to the detn. of H_3PO_4 the results are in large measure dependent upon the quantity of alkali cations present. (5) All of the above methods are compensation methods and accurate results are obtained only with slightly impure ppts. The Schmitz method gives a precipitate which upon ignition yields pure $Mg_2P_2O_7$ and if the conditions are carefully defined the results are accurate. (6) All the methods studied for the detn. of Mg are compensation methods. W. T. HALL

Volumetric determination of sulfuric acid. CARLO PEZZI. *Giorn. chim. ind. applicata* **3**, 10–1(1921).—This is a modification of Raschig's modification of Wolf Müller's method. Prep. a soln. of benzidine by dissolving 2 g. benzidine (base) in ¾ l. H_2O, and adding 3 cc. HCl. When the soln. is limpid, bring to vol. Of this soln. 150 cc. is sufficient for 0.1 g. H_2SO_4. Into the cold soln. of the benzidine-HCl pour the sample to be analyzed. Filter through a Büchner funnel, wash the ppt. on the filter with 15 cc. warm H_2O used in small portions, aspirating each time to dryness, remove the filter papers from the Büchner, place upon a 5 × 15 cm. glass plate, place in a 500-cc. beaker, and wash off with a jet of H_2O. Digest the filter disks in 15 cc. HCl (d. 1.19) and transfer all to the beaker containing the main ppt. (The complete destruction of the paper is necessary in order to obtain the benzidine sulfate which has remained in the paper pores.) When the washing is completed the liquid should have a vol. of about 400 cc. Titrate at 10–12° with 0.05 *N* $NaNO_2$ (prepd. by dissolving 3.4550 g. very pure dry salt in 1 l. H_2O) with starch iodide paper as indicator. The progress of the diazotization is evident from the gradual clarifying of the liquid, which towards the end takes on a perfect limpidness and first a pale lemon then a yellow color. The colored ring on the starch-iodide paper should appear even 15 min. after the last drop is added, in order to assure the completion of diazotization. Each cc. of $NaNO_2$ used corresponds to 0.002452 g. H_2SO_4 or 0.0024015 g. SO_4. Sulfuric acid is pptd. by this method, not only when originally free, but also when present as salts. Sulfates of the heavy metals do not interfere. Compared with gravimetric methods, P.'s method is highly satisfactory, takes 2 hrs. instead of a day, and gives results about 0.2–0.3% below theoretical. ROBERT S. POSMONTIER

Detection and determination of traces of hydrogen peroxide. F. W. HORST. *Chem. Ztg.* **45**, 572(1921).—The test depends upon the oxidation of Fe by means of H_2O_2 and detection of Fe^{+++} with CNS^-. Prepare a 10% acid soln. of $FeSO_4$ in a large Erlenmeyer flask provided with a 3-hole rubber stopper. The first hole serves for a delivery tube through which H_2S or CO_2 can be introduced, the second for the escape of vapor and the third for the withdrawal of the $FeSO_4$ soln.; the first and third tubes dip into the soln. and the first two are provided with glass stopcocks. First

fill the third tube with water to remove air and close the stopcock. Pass H_2S through the cold soln. for some time and then heat to boiling with the stream still passing. Cool in a current of CO_2. In this way Fe^{+++} ions formed by accidental oxidation are surely reduced to Fe^{++}. When the soln. is cold, close tube 2 with rubber tubing containing a piece of stirring rod, and produce a slight excess pressure with CO_2. Meanwhile place about 20 cc. of the soln. to be tested in a test-tube which is marked so that the vol. of additional 2 and 5 cc. portions can be detd. and cover with a layer of about 0.5 cm. of gasoline to prevent oxidation. Allow a little of the $FeSO_4$ soln. to run off so that the pure water is rinsed out of the delivery tube and then run into the test-tube 2 cc. of the soln. After a little while add 5 cc. of concd. NH_4CNS soln. which has been prepared with freshly boiled water. Compare the color thus formed with that produced in the same way with known amts. of H_2O_2. It is important in this test to avoid all chance of oxidation by atmospheric O_2. The CO_2 obtained in cylinders usually contains some O_2 and should be purified by washing with $FeSO_4$ soln. W. T. H.

Combustion analyses with tellurium dioxide. Th. R. Glauser. *Z. angew. Chem.* **34**, Aufsatzteil, 154–5, 157–9, 162–3(1921); *Schweiz. Chem. Ztg.* **1921**, 215–20, 225–9, 238–40.—Fused TeO_2 sublimes only slightly when heated over the blast lamp. Te itself is also slightly volatile. The molten oxide reacts energetically with CaC_2, $CaCN_2$ and even with the relatively indifferent AlN; metallic Te results. Most metals dissolve in the excess of fused or molten TeO_2 with the formation of Te, tellurites and tellurides. Sulfide ores such as FeS, CuS and ZnS likewise dissolve in the TeO_2, forming metallic Te and volatile SO_2. Difficultly fusible glass is attacked but slightly by fused TeO_2. Directions are given for the *prepn. of pure* TeO_2 and for the *recovery of the Te from* the *residues* obtained after combustion. To accomplish an oxidation with TeO_2 a very simple app. is sufficient. This consists merely of an ignition tube of difficultly fusible glass, 8–20 cm. long and 15–18 mm. inside diam. This ignition tube carries a 2-hole rubber stopper through which air freed from CO_2 can be introduced and through which the gas from the combustion can be led into a $CaCl_2$ U-tube and from thence into a weighed absorption tube with KOH or soda lime. To det. the C in Fe or steel about 1 g. of the sample is weighed into the ignition tube and this is followed by at least 9 times as much TeO_2. After connecting up the app. and making sure it is gas-tight, the contents of the ignition tube are gradually heated, finally using the blast lamp. When the stream of gas from the combustion slackens, suction is applied to the front end of the train and the stopcock at the back end is opened so that a slow stream of air is passed through the app. The entire time required for combustion is seldom more than 30 min. The results compare favorably with those obtained with an electric furnace. Compounds rich in Si such as Fe-Si and SiC are attacked with difficulty and it is advizable to heat with a mixt. of PbO and TeO_2 instead of TeO_2 alone. Good results are obtained in the analysis of graphite. The CO_2 content of ores can be detd. similarly by heating with TeO_2 provided no S is present. W. T. H.

The determination of glucose in glucosides. Al. Ionescu. *Bul. soc. chim. România* **3**, 6–9(1921).—The glucoside is subjected to hydrolysis and the resulting glucose detd. by the ferricyanide method (cf. *C. A.* **14**, 3812). Heat about 0.7 g. of the glucoside on the water bath with 50 cc. of water and 2 cc. HCl for 3 hrs. Neutralize with NaOH, dil. to 100 cc. and filter if necessary. Det. the glucose with ferricyanide. Expts. with amygdalin, digitalin and salicin gave results accurate within 0.5%. In the case of digitalin, however, the ferricyanide reacted with the digitalose as well as the glucose itself, both being formed by the hydrolysis. W. T. H.

The determination of dextrose and levulose in solutions. Hans Murschhauser. *Biochem. Z.* **118**, 120–8(1921).—Preliminary expts. showed that levulose does not reduce Fehling-Allihn soln. to as great a degree as does glucose. This fact makes possible a

detn. of the amts. of levulose and glucose in solns. of mixts. of the 2 hexoses when measurement of the rotation of the soln. is likewise made. An example of the method of calcn. makes this clear. 25 cc. of a 1.979% dextrose soln. and 75 cc. of a 1.9941% levulose soln. are mixed and 100 cc. of distd. H_2O are added. 20 cc. of the mixt. give 0.4215 g. Cu_2O = 0.1878 g. dextrose = 0.9390% dextrose: or calcd. as levulose 0.2031 g. levulose = 1.0155% levulose. The α^{20} of a dextrose soln. of above % = +0.9390° in a 189.4 mm. tube. The α^{20} of a soln. of levulose of the above % = −1.7873° in a 189.4 mm. tube. The observed rotation of the soln. analyzed was = −1.065°. Then according to the formula $(a + b) : 100 = a : x$, (where a is the difference between the observed reading and the calcd. on the basis that all the sugar is present as levulose and b is the difference between the observed reading and the calcd. on the basis that all the sugar is present as glucose, while x is the actual dextrose % of the total sugar) $x = \frac{0.722 \times 100}{2.727}$ = 26.48% dextrose and by difference the levulose is 73.52% of the total sugar. That is to say there is 0.2487% dextrose and 0.7466% levulose present in the soln. as analyzed. As prepd. the soln. should contain 0.2474% dextrose and 0.7478% levulose: a difference of + 0.5% for the former and of —16% for the latter. The method is advocated for detns. of the dextrose and levulose content of solns. of mixts. of these hexoses in concns. not above 1%. It is of course necessary to detn. first the reducing power of a 1% levulose soln. in terms of dextrose in order that std. values for computation may be had. F. S. HAMMETT

New method for the determination of formaldehyde. C. KOLLO AND O. LASCAR. *Bul. soc. chim. Romînia* 3, 3–6(1921).—The method depends upon the formation of hexamethylenetetramine by treatment with NH_4OH, the removal of the excess NH_3 by heating, the pptn. of the tetramine by means of a measured vol. of standard picric acid soln. and the titration of the excess acid. Weigh 5 g. of the aldehyde soln. into a 50 cc. calibrated flask. Dil. to the mark and take 10 cc. of the mixed soln. for analysis. Add 5 cc. of pure NH_4OH, d. 0.96, cover the flask with a watch glass and allow it to stand 30 min. during which time the following reaction takes place: $4\ NH_3 + 6\ HCHO \rightarrow (CH_2)_6N_4 + 6\ H_2O$. Heat the soln. over a small flame to drive off the excess NH_3 but do not heat above 60° for fear of decomposing some of the tetramine. When the odor of NH_3 can no longer be detected, transfer the soln. to a 100 cc. calibrated flask. The vol. of the soln. and the washings should amt. to about 25 cc. Add 50 cc. of 0.05 *N* picric acid and dil. to 100 cc. Heat a few minutes and allow to stand 30 min. Filter and take 25 cc. of the filtrate for titration with 0.1 *N* NaOH using methyl red as indicator. The pptn. of the hexamethylenetetramine takes place according to the following equation: $(CH_2)_6N_4 + C_6H_2(NO_2)_3OH \rightarrow [(CH_2)_6N_4.C_6H_2(NO_2)_3OH]$. W. T. H.

Procedure for the detection of fluorescein in very dilute solutions. MAURICE LOMBARD. *Bull. soc. chim.* 29, 462–4(1921).—To detect contamination of potable waters it is a common practice to add fluorescein to the water of which it is desired to follow the course and see if it can be found in another water. It is thus often important to be able to detect the dyestuff in extremely dil. solns. To accomplish this, Trillat has examined the water in tubes a meter long and Diénert has devized an app. which he calls the elec. fluorescope. Fluorescein itself is more sol. in ether than in water but the opposite is true of its salts. Advantage of these simple facts is taken in the following sensitive method for detecting fluorescein. Place 30 cc. of the water in a test-tube, add a few drops of H_2SO_4 and enough ether to give a layer 3 or 4 mm. deep on top of the water. Shake and allow to stand. When the ether is well separated add a few drops of NH_3 soln. and gently shake to mix with the ether. Look at the ether layer against a dark background, turning the test-tube toward the light. The ether will appear greenish if the test is positive. On allowing to stand, the color of the NH_4 salt slowly passes

into the water. One part of the dyestuff in 200,000,000 of water can be detected. Or, 1 part of dyestuff in 500,000,000 can be detected as follows: Shake 200 cc. of acidulated water with 30 cc. of ether. Drain off all but a few cc. of the water and evap. the ether from an extraction flask. Transfer the residue to a test-tube and test with acid, ether and NH_3 as above. W. T. H.

Simultaneous detection of tartaric, oxalic and formic acids with resorcinol and sulfuric acid. F. KRAUSS AND H. TAMPKE. *Chem. Ztg.* **45**, 521(1921).—These 3 acids all give colorations when treated under proper conditions with resorcinol and H_2SO_4 but the color rings obtained when the 3 acids are present occur at different parts of the test-tube, formic acid on top, oxalic acid in the middle and tartaric acid at the bottom. To test for the 3 acids, dissolve 0.2 g. of pure resorcinol in 5 cc. of the soln. to be examd., which should be faintly acid with H_2SO_4. Add carefully 10 cc. of concd. H_2SO_4. If the 3 acids are present, CO is evolved and an orange ring, gradually broadening, shows the presence of formic acid; a narrow blue ring below the orange ring shows the presence of oxalic acid. Carefully heat the bottom layer of H_2SO_4 in the test-tube, but take care not to heat the rings. Under the blue oxalic acid ring, a third deep red ring is produced by the tartaric acid. In carrying out the test CO_3^{--}, S^{--}, I^- and Br^- should be absent. Oxidizing agents are also harmful and can be removed by boiling with H_2SO_3 or by treatment with Zn and dil. H_2SO_4. W. T. H.

Thallous ferricyanide (determination of thallium) (CUTTICA, CANNERI) **6**. A decomposition of nitrous acid (OLIVERI-MANDALÀ) **6**. Absorption of carbon monoxide in a current of air (DESGREZ) **2**.

ARTMANN, PAUL and HANOFSKY, KARL: **Kurze Anleitung zur qualitativen chemischen Analyse.** Leipzig and Vienna: Verlag Franz Deuticke. For review see *Oesterr. Chem. Ztg.* **24**, 94(1921).

MÜLLER, ERICH: **Die elektrometrische Massanalyse.** Dresden and Leipzig: Theodor Steinkopff. 110 pp. For review see *Chem. Weekblad* **18**, 409(1921).

REEVE, FREDERICK, C.: **Elementary Qualitative Analysis of the Metals and Acid Radicals.** New York: D. Van Nostrand Co. 143 pp. $1.50. For review see *Eng. Mining J.* **112**, 18(1921).

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Compiled by R. E. Doolittle *et. al.* Washington, D. C. Association of Official Agricultural Chemists. For review see *Chem. Met. Eng.* **24**, 982(1921).

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

Jurupaite, a new mineral. ARTHUR S. EAKLE. Univ. Cal. *Am. Mineral.* **6**, 107–9(1921).—This mineral, named after the mountains in which the locality, Crestmore, lies, forms compact aggregates of white radiating fibrous spheres, resembling pectolite. H. = 4, sp. gr. = 2.75. It is probably monoclinic, and has the *ns.* // elongation 1.576 and ⊥ elong. 1.568. It fuses easily to a clear glass and is easily sol. in HCl without gelatinization. Mean of 2 analyses: SiO_2 48.87, CaO 38.66, MgO 4.19, H_2O 7.89, corresponding to $2(Ca, Mg)\,O.2SiO_2.H_2O$, with CaO:MgO = 7:1. It is believed that the Mg is an integral part of the mineral because of the localized crystn. The H_2O is tenaciously held, so that the formula should be written $H_2(Ca, Mg)_3Si_2O_7$. The mineral is thought to have been deposited by orthosilicic solns., like other fibrous Ca silicates of the deposit. E. T. W.

Inyoite from New Brunswick. EUGENE POITEVIN AND H. V. ELLSWORTH. Canada

Dept. Mines, Geol. Survey *Bull.* **32**, 21 pp.(1921).—This rare mineral, heretofore found only in Cal., has been obtained in a gypsum quarry at Hillsborough, N. B. It is in brilliant crystals rich in forms, of which $a(100)$, $z(120)$, $k(011)$, $v(021)$, $i(\bar{1}01)$ $h(\bar{2}01)$, $y(\bar{1}11)$ and $g(\bar{3}12)$ are new. The axial values are $a:b:c = 0.8833:1:0.6950$; $\beta = 65° 59'$. The $n_\beta = 1.501$ and sp. gr. = 1.885. It is readily sol. in dil. acids and partially in H_2O; it loses part of its H_2O of crystn. when heated under H_2O, showing its temp. of formation to have been very low. Somewhat over 32% of the H_2O goes out below 110°, the balance only at red heat. Methods of analysis are given; results were: CaO 20.42, B_2O_3 37.44, SO_3 0.55, H_2O −32.46, H_2O +9.46, sum 100.33%, which after deducting gypsum indicates the formula $2CaO.3B_2O_3.3H_2O+10\ H_2O$.

L. W. Riggs

The importance of salt petrography in potash mining. F. von Wolff. *Jahrb. Halleschen Verband. Erforsch. Mitteldeut. Bodenschätze* **1919**, 15–21; *Expt. Sta. Record* **44**, 322.—The petrography of the German potash deposits is discussed. It is shown that data on the petrography of the salt deposits serve to indicate the mineralogical compn. of the natural salt profile, and with the aid of the theoretical knowledge of transformation processes indicate those transformations undergone by the deposits. This information is considered to be of great practical value, since the potash miner must know whether valuable leachings have been removed and where they have gone. An exact knowledge of the contents of the salt deposits should also be of practical importance in this connection H. G.

The action of certain rock formations on petroleum. E. Longobardi. *Anales soc. quim. Argentina* **7**, 418–21(1919).—Much of the petroleum of the Argentine Republic has been more or less altered by contact with the rock formations through which it has filtered. Some samples are very fluid and light colored probably owing to percolation through fuller's earth or similar material. Others contain small amts. of dissolved V compds. Still others show optical rotation possibly due to org. substances dissolved from fossil-bearing strata. L. E. Gilson

Petroleum genesis and geology, setting forth concurrent conditions. S. F. Hunt. *Salt Lake Mining Rev.* **23**, No. 6(1921).—A detailed article dealing with the genetic factors involved in the origin of petroleum deposits. A. H. Heller

The igneous rocks of Sviatoy Noss, Transbaikalia. Pentti Eskola. Univ. Helsingfors. *Översikt. Finska Vetenskaps. Soc. Förh.* **63A**, No. 1, 99 pp.(1921).—The region is underlain by 2 great rock complexes, a granite-granodiorite mass, and injected cryst. schists (migmatite). Among the igneous rocks is a remarkable and raditebearing syenite named *sviatonossite* after the locality. Analyses are given of 2 granodiorites, with calcn. of the norms and the Osann values. One of these appears to possess a primary consolidation structure, but critical examn. shows that the hornblende, though apparently the first mineral to crystallize out, has really originated at the expense of still earlier diopside, biotite, and probably olivine. This is undoubtedly a more wide-spread phenomenon among rocks in general than is usually recognized. An even-grained granite was also analyzed, and norms and Osann values were calcd. Aplite and kersantite were similarly studied, and when averaged in the ratio, based on observed frequence, of 5:3, the resulting compn. was essentially identical with that of the granodiorite, showing that the 2 dike rocks have originated by differentiation of the granodiorite magma. Pegmatites of somewhat unusual mineralogical compn. are described. The new rock sviatonossite is described in detail, analysis giving: SiO_2 58.55, Al_2O_3 15.62, Fe_2O_3 3.02, FeO 2.57, MnO 0.17, MgO 1.14, CaO 7.34, Na_2O 5.11, K_2O 4.16, TiO_2 0.92, P_2O_5 0.49, H_2O 0.26, sum 99.35%. Analyses were also made of the garnet and diopside sepd. from the rock. Analysis of an andradite garnet from skarn rock enclosed in an aplitic granite was also made, and on comparison with analyses of

andradites from other skarns, it is found that the compn. of the garnet of the sviatonossite is quite close to that of skarn garnets in general. It is less like andradite garnets of igneous origin, and is believed to have originated under physical conditions almost identical with those prevailing at the formation of the skarn rocks; although the crystn. of andradite has been rendered possible by the peculiar chem. compn. of the magma, no matter how this peculiarity originated. The pyroxene of the sviatonossite belongs to the aegirite-augite series, but differs radically from typical skarn pyroxenes, sharing the properties of pyroxenes from moderately alk. igneous rocks. An aplitic phase was also analyzed and studied. It contains epidote, intergrown with quartz, probably explainable on the basis of low temp. of crystn. of the magma. An aegirite-augite granite was studied similarly. The relations of the sviatonossite to other igneous rocks are considered at length, many analyses being quoted. It is most nearly related to malignite and borolanite. Consideration of the contact phenomena indicates that the sviatonossite owes its peculiar compn. to assimilation by the granite magma, of limestone, or more probably of skarn first formed from it. This upholds Daly's theory of the origin of alk. rocks. E. T. W.

Metasomatic changes in silicate rocks. PENTTI ESKOLA. *Norsk geol. Untersök.* **6**, 89–107(1920).—A further discussion of some of the data described in *C. A.* **9**, 1161. Granite batholiths acting on leptites have greatly altered the compns. of the latter, there having been an addition of Mg, Fe, Si, H, Al?, S, As, Cu, Zn, Pb, Au and Bi, and a subtraction of Ca, Na, K?, and CO_2. Not only the carbonates but also the silicates have suffered alteration on a large scale, and the addition of Mg besides Fe plays a dominant role. A tabular classification of silicate metasomatism and the resulting rocks is presented. E. T. W.

Character, age, and cause of rock metamorphism in Graubünden. RUDOLF STAUB. *Vierteljahrs. Naturforsch. Ges. Zürich* **65**, 323–76(1920).—In this region basic rocks are represented by peridotite and amphibolite; serpentine is almost absent. The biotite gradually disappears in upper strata while quartz, feldspar, and muscovite gradually appear. Four periods in which contact metamorphism has occurred have been established. Mesozoic contact metamorphism was the first, but has been changed by all later metamorphisms. Contact metamorphism of the carboniferous is confined to narrow, broken seams in lower East Alpine strata. Monzonite, banatite, diorite, essexite, and granite are typical rocks while clinozoisite, zoisite, epidote, titanite, garnet, orthite, biotite, hornblende, and muscovite appear. Contact metamorphism of pre-carboniferous is established by zone formation of eruptive rocks running across the early carboniferous massif and appearing mylonitized and exfoliated. Dynamic metamorphism of lower strata is concealed by effects of regional metamorphism but is identified by mylonitization. Each period of folding has been accompanied by mechanical metamorphism and connected with each are enormous magma bodies. A period of intrusion followed each and caused far reaching contact metamorphism. Regional metamorphisms in 3 localities are described. Tabulation of metamorphism indicates a cycle of the 3 kinds. The causes are stratigraphic and tectonic, overhead stoping, and sinking of geosynclinals. Regional metamorphism is not a result of contact metamorphism as shown by this region, but the former produced conditions for the latter. At great depths the two conceal each other. Assimilation and differentiation are of equal importance and work together in a concealing magma. G. R. JACKSON

The data of geochemistry. F. W. CLARKE. *U. S. Geol. Survey Bull.* **695**, 832 pp. (1920); *Expt. Sta. Record* **43**, 419.—This is the 4th edition, revized and enlarged, of this important work (*C. A.* **10**, 1487) dealing with the compn. of the earth's crust, waters, and atm. "To bring some of the data together, to formulate a few of the problems, and to present certain general conclusions in their modern form are the purposes

of this memoir. It is not an exhaustive monograph upon geochemistry, but rather a critical summary of what is now known and a guide to the more important literature of the subject." It contains data of very great importance from the standpoint of agricultural science. H. G.

Presence in meteorites, gems, ores, quartz, granite, basalt, volcanic ash and lavas of "organites" susceptible of revivescence, and resistance to high temperatures. V. GALIPPE AND MME. G. SOUFFLAND. *Compt. rend.* **172**, 1252–4(1921).—In a previous study upon fossils the samples were heated to temps. ranging between 200° and 340° to insure the impossibility of microörganisms penetrating from the exterior. The same technic applied to more than 50 samples of the minerals mentioned in title shows that each contains "organites" capable of reviving and multiplying. Direct microscopic examn. revealed the constant pressure of ovoid corpuscles, generally endowed with movement, which in the cases of quartz and lava ash samples was very lively. L. W. R.

Tsunashiro Wada. GEORGE F. KUNZ. *Am. Mineral.* **6**, 109–13(1921).—An obituary notice of the eminent Japanese mineralogist. E. T. W.

The siliceous rocks considered from the viewpoint of manufacture of silica bricks (BERTRAND, LANQUINE) **19**. Magnetic susceptibility of certain natural and artificial oxides (HERROUN, WILSON) **2**. Exchange of ions on the surface of minerals (TAMMANN) **2**. The genesis of a fertile soil (HARRISON, ANDERSON) **15**. The clays of the Tandil Mts. (ZAMBONNI) **19**.

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The metallurgy of zinc in Mexico. The calcining and smelting plant for zinc ores of the International Ore and Smelting Co. at Saltillo, Mexico. G. MONTES DE OCA. *Bol. minero* **11**, 492–500(1921).—A description of the plant of the Belgian-owned International Ore Co. The plant has been operated commercially only for the calcining of carbonate ores but distn. furnaces are under construction and a plant for treating blende is projected. The ore treated has the compn. 4.5% Pb, 18.5% SiO_2, 5.7% Fe, 5.5% CaO, 32.6% Zn. R. S. DEAN

Queen nine-hearth roaster. J. MOORE SAMUEL. *Trans. Am. Inst. Met. Eng.* No. **1079-N**, 12 pp.(1921).—A discussion of a nine-hearth roaster designed at the plant of the Copper Queen Reduction Works. H. C. PARISH

Principles of leaching and precipitation of copper. FRANK E. LATHE. *Can. Chem. Met.* **5**, 202–3(1921).—While in recent years oil flotation has largely replace leaching, there are still 6 principle leaching plants in America. The preliminary treatment of the ore consists in either roasting, crushing, or desliming, depending upon the character of the ore. It is then treated with a solvent. Probably 75% of leaching is done with H_2SO_4, although NH_4OH and $(NH_4)_2CO_3$ also are used. The Cu is then removed either by electrolysis or pptn. on scrap iron. H. C. PARISH

Constitution of gas atmospheres in aluminium alloy melting furnaces. ROBERT J. ANDERSON AND J. H. CAPPS. *Chem. Met. Eng.* **25**, 54–60(1921); cf. *C. A.* **15**, 2815.—A tabulation and discussion of the compn. of gases in contact with the metal in various types of Al-melting furnaces. H. C. PARISH

Note on Schwartz furnace atmosphere when melting complex bronzes. R. J. ANDERSON AND J. H. CAPPS. *Chem. Met. Eng.* **25**, 103(1921).—A summary of analyses of the gases within a Schwartz furnace melting leaded Zn bronze and Pb brass shows wide variations in CO_2, CO, N, and O content with the combustion more complete than in Al-alloy melting furnaces (cf. preceding abstr.) W. H. BOYNTON

Metallurgical requirements of brass melting equipment. T. H. A. EASTICK. *Brass World* **17**, 208–9(1921).—E. blames the design of melting equipment for most Cu and Cu-alloy failures. The melting operation should be effected by rapid and uniform heating to the pouring temp., by prompt pouring, by maintaining thorough stirring, and by keeping the metal clean and free from slag and dirt. Greater speed and uniformity of metal are obtained by heating from the bottom unless a rotating or rocking motion is imparted to the mass. The necessity of the careful study of conditions, costs and the fuel problems is emphasized. W. H. BOYNTON

A type of natural draft melting furnace. I. C. VICKERS. *Brass World* **17**, 197–201(1921).—V. describes an installation of the natural draft type of melting furnace and points out its utility in small foundries and under certain conditions. The elevation of the furnace, its location and construction, and the materials required are discussed. W. H. BOYNTON

Electricity in the tinplate industry. L. ROTHER. *Engl. Elec. J.* **1**, 190–8(1921).—An illustrated detailed account of modern tinplate manuf. C. G. F.

The pig iron industry of Oregon. WM. H. CRAWFORD. *J. Elec. Western Ind.* **47**, 109–10(1921).—A historical sketch. A photograph is shown of an old stone furnace built in 1866. No pig Fe has been made in Oregon since 1893. The Pacific Coast consumption is 100,000 tons of pig Fe per annum (a large proportion of which now is imported from Belgium). C. strongly recommends the revival of the industry in Oregon. Full details are given. C. G. F.

The iron and steel industry of India. J. COGGIN BROWN. *Mining Mag.* **24**, 339–47; **25**, 11–9(1921).—A detailed account of the historical development and present extent, including ore deposits, works, and metallurgical methods. A. BUTTS

Cupola daubing clay affects iron. CARL BUBERL. *Foundry* **49**, 533–4(1921).—B. explains at length various mixts. of Al filings and fireclay for daubing cupolas. He also discusses the theory of S combinations in gray iron castings and the influence of the fireclay on the Fe indirectly through the S. E. G. JARVIS

Discussion on open hearth practice. HENRY WM. SELDON. *Blast Furnace & Steel Plant* **9**, 422–3(1920).—A discussion of considerations in drying out and heating up an open-hearth furnace, life of the furnace, utilization of heat, and output per hour. Hot furnace walls do not mean efficient working, but proper absorption of heat by the charge is necessary; a poorly working furnace will sometimes have the highest temp. Extra time in thorough drying out and slow heating pays in the end. A. BUTTS

The addition of fluorspar to open hearth steel furnaces. S. SCHLEICHER. *Stahl u. Eisen* **41**, 357–61(1921).—The fluorspar added to the slag is only slightly decompd. Silica is vaporized from the slag as silicon fluoride and is replaced with silica from the furnace lining. Fluorspar has a desulfurizing effect, the sulfur being driven out of the slag and the slag taking up more S from the bath. R. S. DEAN

Influence of basicity of the slag on the operation of the basic converter. L. BLUM. *Stahl u. Eisen* **41**, 69–71(1921).—The basicity of the basic converter slag is the content of free lime which is obtained by subtracting the sum of the lime to combine with the P as tetra-calcium phosphate and with the silica as calcium singulo-silicate from the total lime. The most economical dephosphorization and desulfurization takes place when the excess of lime is 4%. R. S. DEAN

Purification of blast furnace gas. A. GOUVY. *Rev. metal.* **17**, 677–86(1920).—G. describes the Cottrell process for the purification of blast furnace gas by means of the high tension elec. current. The advantages of it over the wet method and the dry-filter method are: no loss in calories of the gas; avoidance of the enormous loss of water for cooling purposes; no unutilizable mud residue; no corrosion of the refractory material by the dusts; the recovery of the sol. potash contents of the dust; the entire

absence of the filter sacks which deteriorate and force shutting-down the plant for repair or renewal; and the use of a perfectly clean gas as fuel for stoves, boilers or gas engines. J. L. WILEY

The elastic limit. WM. ERNEST DALBY. *Engineering* 112, 81(1921).—From a practical point of view, the term elastic limit should mean the limit where proportional elasticity ends and unproportional elasticity begins. Unloading from any load below this limit and reloading can be done without describing a hysteresis loop. Unloading and loading, once the limit has been passed, is always accompanied by an elastic hysteresis loop. V. O. HOMERBERG

Hardness testing of metals. WHITTEMORE, ET AL. *Mech. Eng.* 43, 445–9(1921).—Report of a committee of the engineering division of the National Research Council on various methods of testing the hardness of metals. The hardness obtained with a Morin hardness tester is not affected to any considerable degree by the amt. of energy of impact. Too light a blow is likely to give more erratic results than a heavy blow, and as the correct measurement of the diam. of a small indentation is difficult, the diam. of the impression should not be smaller than 2.5 or possibly 3 mm. The hardness of the standard cube should be as near to that of the specimen as possible. A difference in hardness amounting to more than 50 Brinell units would be likely to make the error exceed 10%. It is possible that this limitation might be removed by the use of an appropriate correction formula, but this would still further complicate the use of the app. The size of the standard cubes is too small to obtain their Brinell hardness accurately. They are distorted by the 3000-kg. load more than larger blocks would be. Owing to the fact that each block can be used for only 6 readings, the time and expense required to make additional blocks is a rather serious restriction on the use of the app. The proximity of the hardness of the standard cube to that of the specimen to be tested is numerically of greater importance in the case of hard material than in the case of soft. With respect to the Brinell meter, the dimensions of the standard bars are so small as to cause error in measuring their hardness in the usual manner. It would seem that the cross-section of at least twice the dimensions would be preferable. A variation in the applied load causes a slight change in the hardness number. A table is given to show that in most cases for the static load tests the Brinell meter hardness was practically identical with the Brinell hardness if the standard load of 3000 kg. was used. Both values decrease with decreasing loads, and the decrease in the Brinell hardness emphasizes the necessity for using the standard load of 3000 kg. for hard, and a load of 500 kg. for soft metals. The errors in the Brinell meter hardness due to variations in load are less than for the Brinell hardness. The greatest accuracy is obtained when the diam. of the indentations for the Brinell meter is approx. that obtained on the same material in a Brinell testing machine under standard load. The celluloid scales should not be used to measure the diam. of the indentations. A micrometer microscope graduated to tenths of a mm., which division allows hundredths of a mm. to be easily estd., will be found suitable for the purpose. V. O. HOMERBERG

Application of the scleroscope to the determination of the hardness of thin brass strip. G. H. BLENKARN. *J. Inst. Metals* 25, 345–6(1921).—In using the scleroscope with the magnifier hammer for the detn. of the hardness of annealed thin brass strip below 0.013 in. thick, the readings become higher as the thickness is reduced. A reading of 38 is obtained instead of 14.5 on soft annealed brass of a thickness of 0.003 in., owing, undoubtedly, to anvil effect. In using 2 pieces the hardness reading remained normal for thickness down to 0.007 in., below which the readings again increased, owing to anvil effect. Below 0.007 in. thick by using 3 pieces normal readings were obtained down to a thickness of 0.004 in., below which thickness the anvil effect still became evident. From a study of a diagram presented, it would appear that

for annealed thin brass strip satisfactory readings cannot be obtained with a less thickness of metal than 0.013 in. between the hammer and the anvil. For thin hard brass strip the errors due to anvil effect are not so marked as with annealed strip, even at the lowest thickness experimented on, *viz.* 0.003 in. V. O. HOMERBERG

Study impact tests on cast steel. F. C. LANGENBERG. *Foundry* **49,** 512–4, 519 (1921).—Results are given of investigations of impact tests on cast steels of varied compns. and heat treatments. A higher shock strength was obtained on the low-P material. An increase in the P content from 0.043 to 0.104% decreased the shock strength by some 53%. A curve is given to show that the Charpy value has a decided relationship to the P content. The most decided decrease or falling off of the Charpy value occurs when the P content is increased beyond 0.06%. All of the material was poured from 1 melt, and all conditions, excepting the P content, were maintained const. Several tables of Charpy and Brinell tests as well as photomicrographs are included. V. O. HOMERBERG

Physical tests of sheet nickel silver. WM. B. PRICE AND PHILIP DAVIDSON. *Chem. Met. Eng.* **25,** 141–8(1921).—A study was made of the physical properties of sheet nickel silver when subjected to cold-rolling and when annealed at a variety of temps. extending from 350° throughout the commercial heating range. Four alloys of the following compn. were used:

	Cu.	Pb.	Fe.	Ni.	Mn.	Zn.
Alloy *A*	64.68	trace	0.194	6.73	0.06	remainder
Alloy *B*	65.82	1.27	0.227	6.17	0.06	remainder
Alloy *C*	65.44	trace	0.345	17.83	0.08	remainder
Alloy *D*	65.60	1.08	0,238	17.77	0.06	remainder

The results are tabulated and represented graphically. The nickel silvers with the lower Ni content were slightly harder than brass subjected to similar treatment. The nickel silvers with the higher Ni content, although slightly harder when in the annealed condition, do not harden as rapidly under severe cold-rolling as those with the lower Ni content. The presence of 1% Pb in any alloy tested did not appear to affect the physical properties to any great extent. Nickel silver is similar to brass with respect to its grain characteristics excepting that grain growth is retarded by the presence of Ni. Severely worked material with the lower Ni content —alloys *A* and *B*—showed a beginning of recrystn. at 350°, which is about 50° higher than in the case of brass. In the nickel silvers with the higher Ni content—alloys *C* and *D*—the first signs of recrystn. on the hard-rolled specimens was observed at 500°. The effect of Ni is to raise the tensile strength and lower the % elongation. Several photomicrographs are given to show that in order to attain a given grain size the 18% nickel silver requires an annealing temp. about 100° to 150° higher than will suffice in the case of the 7% Ni alloy. V. O. HOMERBERG

Properties of antimonial lead. LOUIS J. GUREVICH AND JANE S. HROMATKO. *Chem. Met. Eng.* **25,** 62–3(1921).—M. p. detns. are too indefinite to be used as a basis for calcg. the compn. of Pb-Sb alloys. The addition of Sb increases the hardness of the alloy. The max. tensile strength of the Pb-Sb alloys is reached with an alloy containing 10% Sb. The alloy containing 4.5% Sb gives the greatest reduction of area and is the most ductile. V. O. HOMERBERG

Electric furnace *vs.* oil-fired furnace for hardening tools. H. W. DERRY. *Elec. World* **78,** 276(1921).—Comparative costs show the elec. furnace to be the cheaper. C. G. F.

Heat-treatment of high-speed cutting tools of intricate design. A. J. LANGHAMMER. *Chem. Met. Eng.* **25,** 30(1921).—L. believes that the open-fire hardening method (any

method employing a muffle, or semi-muffle furnace, or a blacksmith's forge) is superior to the pack-hardening method, and further states than an intricate cutting tool which has been correctly hardened by the open-fire method will permit greater cut speeds, longer periods between regrinds, produce a finer product, give a longer life, and, therefore, will yield a bigger production at reduced factory costs. V. O. HOMERBERG

Industrial control of the extent of case hardening by means of quenched test pieces. J. GALIBOURG AND M. BALLAY. *Rev. Metal.* **17**, 216–21(1920).—The common practice in controlling the extent of case hardening is to place in the containers soft iron test cylinders, which are withdrawn from time to time and examd. in the following way. The cooled pieces are reheated to about 800°, quenched and broken, and the depth of cementation is estd. by measuring the depth of the outer zone, consisting of fine grains, while the unaltered center consists of large brilliant grains. This method is inexact in that the extent of reheating affects this grain size and consequently test pieces are occasionally obtained which show no outer zone; and also because an intermediate zone interferes with a precise estn. It is out of the question, because of the time involved, to grind and polish such test pieces for the usual metallographic examn., but it has been found that such pieces quenched from 800° as taken from the boxes may be broken, treated with a copper reagent which deposits selectively upon the soft iron core, and the cementite zone examd. directly with the usual 10 times Brinell test microscope. The reagents recommended are those of Stead and LeChatelier-Dupuy. (1) Stead reagent MeOH, 100 cc., H_2O 18 cc., HCl 1 cc., $CuCl_2.2H_2O$ 1 g., $MgCl_2.6H_2O$ 4 g. (2) LeChatelier-Dupuy reagent. EtOH (95%) 100 cc., H_2O 10 cc., HCl 1 cc., $CuCl_2.2H_2O$ 1 g., picric acid 0.5 g. (3) Denatured alcohol 100 cc., HCl 1 cc., $CuCl_2.2H_2O$ 2 cc., (4) EtOH (95%) 100 cc., HCl 1 cc., $CuCl_2.2H_2O$ 1 g. These reagents give similar results but (4) is not so clear-cut as the first three. The results obtained by this method are considerably more exact than those obtained in the usual way. STANLEY L. CHISHOLM

The oxidation of carbon tool steel on heating in air. HOWARD SCOTT. *Chem. Met. Eng.* **25**, 72–4(1921).—In the tests were used Armco Fe in the form of ½-in. plate and steel in the form of 1-in. round bar of the resp. compns.: C 0.03, 0.86; Mn 0.06, 0.51; Si trace, 0.04; S 0.021, 0.040; P 0.004, 0.024. The method of treatment and prepn. is given. The data obtained showed that the scaling of the Armco Fe is greater than that of the steel under identical conditions, owing to the greater affinity of the O for the C than for Fe. The size of the specimen is immaterial under the conditions of the expt. except when it is less than ⅛ in. thick. The same depth of decarbonization does not imply the same amt. of C lost; thus ½ hr. at 1060° gives the same depth of decarbonization as 1 hr. at 970°, although the microstructure shows less free ferrite in the latter case. Below about 850° and for a period up to 5 hrs. there was no appreciable decarbonization; that is, scaling at least keeps up with decarbonization. V. O. HOMERBERG

Tempering and annealing of metallurgical products. I. Effects and conditions of tempering. LEON GUILLET. *Rev. gen. sci.* **31**, 432–41(1920). **II. The relation between the theory of alloys and the phenomenon of tempering.** *Ibid* 473–87.—G. discusses in detail the theory of alloys as it is applied to solid solns. of various types, with and without allotropic transformations. This section is illustrated with the usual diagrams. He then considers the effects of heating to and cooling from various temps., showing the connection between the results obtained and the diagrams. G. also discusses those cases in which the transitions take place at different temps on heating and cooling and describes the effects of this hysteresis on the tempering. **III. The effect of sudden cooling on structure.** *Ibid* 523–47.—The effects of quenching on the metallographic constituents of steel and bronze are discussed in detail, including

changes in physical properties commonly associated with these structure changes, together with the effects of added elements on the lowering of the critical temp. Many photomicrographs are given. **IV. Annealing.** *Ibid* 564–81.—A detailed summary is given of the available information regarding the general effects of annealing and the properties of annealed material. As in the earlier sections many photomicrographs are given. R. S. W.

Quenching and drawing metallurgical products. V. General conclusions LEON GUILLET. *Rev. gen. sci.* **39**, 614–20(1920); cf. preceding abstract.—The structure of a heat-treated steel or alloy depends upon the compn. of the metal, method and temp. of heating, quenching and drawing. It is seldom possible with steels to produce one structure to the exclusion of all others. Ordinary carbon steels are never austenitic. The different structures correspond very closely to Ar_1, Ar_2, and Ar_3. Pearlitic steels are softest, martensitic steels give max. hardness, and others are intermediate. Hot and cold work influence phys. properties similarly to quenching and drawing, although the microscope shows difference in structure. For commercial heat-treating the temp. of heating is detd. by compn. of steel, and the time by the size of the specimen. The quenching medium must provide quick but not too rapid cooling, depending upon the kind of alloy steel. The drawing temp. is selected to give the desired phys. properties. In this operation the temp. should not exceed 600° and great care should be taken to produce homogeneity. Diagrams are given to show difference in homogeneity before and after drawing on shells made during the war. Several curves show the variation in Brinell hardness, using a 10-mm. ball and a 3000-kg. load, from center to edge of Ni-Cr steel bars, 7 mm. in diam., which were quenched in water and in oil from 750° to 900°. Water-quenched samples are harder, and higher temp. gives greater hardness. Similar curves show the relation of compn. of steel to the method of heat-treating, when using ordinary C, Ni, Ni-Cr, and Mn-Si steels. They were quenched in air, water and oil from 850° to 875° and drawn at 550°. Mn-Si steels show greatest and Ni-Cr self-hardening steels the least variation. No analyses are given. More data on the relation of work to quenching and drawing, the effect of expansion and magnetism, the differences between steel Al and Pb alloys, and the Fe-C diagram will insure a better coöperation between laboratory and factory heat-treating. Different theories of quenching and drawing are briefly discussed. W. A. MUDGE

The Ar_3 point and martensite. P. DEJEAN. *Compt. rend.* **171**, 791–4(1920); cf. *C. A.* **11**, 2882, 3221; **14**, 524.—It is shown that the results obtained by Guillet (cf. preceding abstract) can be made to harmonize with statements already advanced by D. in earlier work. To obtain more information on the general subject, D. has detd. for relatively slow rates of cooling the position of the Ar_1 and Ar_3 *critical points of Mn steel* for Mn contents of from 0 to 14%, and for C contents of 0.2, 0.3 and 0.6% in the case of Ar_3 and of 0.3, 0.6, 0.9, and 2.0% in the case of Ar_1. Mn steel was chosen instead of Ni steel, to avoid the complicating thermal effects which occur in the latter due to the sepn. of graphite. The 2 cases are analogous, however, in so far as the phenomena under consideration are concerned. The exptl. measurements are presented in the form of curves in which critical temp. is plotted as ordinate and Mn content as abscissa for the different C parameters. The Ar_3 point is lowered by the addition of Mn much more rapidly than is the Ar_1 point, so that the two sets of curves intersect. For suitable compns., therefore, the Ar_1 point is reached before the Ar_3 point. If nothing opposes the pptn. of cementite it occurs at the proper temp. and is able at the same time to drag along with it the Ar_3 change owing to the introduction of a new component into the system. Passive resistance, however, may operate to cause the Ar_1 transformation to be incomplete. If in such a case the normal Ar_3 point is below Ar_1, allotropic transformation at the latter temp. occurs only to a small extent but is com-

pleted when Ar_3 is reached without causing the pptn. of the cementite which still remains in soln. If the pptn. of cementite is entirely prevented at Ar_1 it remains in soln. without affecting the Ar_3 transformation, which occurs at a lower temp. In this way pure martensitic steel is obtained, which, as LeChatelier has pointed out, is composed of Fe carbide in soln. in alpha Fe. A. L. FELD

Artificial seasoning of steel. H. J. FRENCH. *Chem. Met. Eng.* **25**, 155–8(1921).—A review of available data on length changes and spontaneous generation of heat in hardened steels, together with results of preliminary expts., on artificial seasoning by different methods of several types of steels used for making limit gages. V. O. HOMERBERG

High-temperature-resisting alloys for carburizing. A. BENSEL. *Trans. Am. Soc. Steel Treating* **1**, 598–601(1921).—A new alloy contg. Ni 60%, Cr 12%, Fe 26% and Si, Mn and C 2%, m. 2660° F., d. 8.15, sp. heat 0.111 at 100° C., coeff. of expansion 0.000121 from 0° to 100° C., thermal cond. 0.0341, elastic limit (cast) 40,000, tensile strength (cast) 54,000, elongation (cast) 1.0%, reduction of area (cast) 2.5%, and Brinell hardness (3000 kg.) 179. W. A. MUDGE

Comparative tests of steels at high temperatures. R. S. MACPHERRAN. *Chem. Met. Eng.* **24**, 1153–5(1921).—From a series of tests made, it was believed probable that there is no one temp. at which all steels will show a decided change in physical properties; this point will vary in steels of different compns. or treatments. The max. tensile strength for rolled C steel, annealed, and forged 3.25% Ni steel, annealed, occurs between 600° and 650° F. The max. tensile strength usually occurs at a higher temp. than the minimum ductility. Most of the tensile-strength curves, especially those of heat-treated steels, drop sharply as the temp. exceeds 800° F. The effect of Ni in small amts. was found to be slight, but in large amts. it tends to lower the temp. at which tensile strength begins to decline. Steel containing Ni was also the only steel examd. in which the ductility materially diminishes at the higher temps. The same property was observed in a set of Monel-metal bars that had been forged. The alloy steels containing Cr are less affected by rise in temp. than C steels. The curves of the tensile loads, elongation and reduction all ran out more nearly straight than in C steels and the max. loads occurred at higher temps. The C steels were not heat-treated and it is possible that quenching and tempering would alter the shape of these curves. The results obtained indicated that the introduction of metals forming carbides tends to strengthen steels at high temps. V. O. HOMERBERG

A suggested method for determining the comparative efficiency of certain combinations of alloys in steel. J. D. CUTTER. *Trans. Am. Soc. Steel Treating* **1**, 188–90 (1920).—From data on Cr-Mo, Cr-V, high-Cr-Ni, low-Cr-Ni, and 3.5% Ni steels, C. derives formulas, (1) Efficiency = Merit index ÷ expenditure for alloys, and (2) Merit index = (Elastic limit − breaking strength × Elongation) ÷ 2/(100 − reduction in area). These are general only but offer interesting possibilities for comparison. Cr-Mo steels have highest Merit index and efficiency. W. A. MUDGE

Alloy steel. Its rise and secrets. A. E. WHITE. *Trans. Am. Soc. Steel Treating* **1**, 481–99(1921).—A general discussion of the relations between chem. compn., physical properties and constitution of Ni, Cr, V, Mn, Mo, Si, W, Ni-Cr, Cr-V, Cr-Mo, Si-Mn, Cr-W steels. For comparison calcns. are made to Ni basis. W. A. MUDGE

Properties and microstructure of heat-treated non-magnetic, flame-, acid-, and rust-resisting steel. CHARLES M. JOHNSON. *Trans. Am. Soc. Steel Treating* **1**, 554–75 (1921).—A study has been made of high-Cr, high-Cr-Ni, high-Cr-Si, 25%-Ni, 38%-Ni and Cu steels, wrought iron and Monel metal. Complete physical data are given together with photomicrographs which show typical structures. Corrosion tests with several

acids and salts, and resistance to oxidation at 1760° F. indicate unique opportunities for this new steel. No analyses are given. W. A. MUDGE

Factors governing the production of heated products. J. A. BROWN. *Trans. Am. Soc. Steel Treating* **9**, 575–87(1921).—The selection of equipment and fuel must be made on a basis of plant conditions. The heat-unit standard is not a real test of the value of a fuel, nor is the heat balance a real test of the value of equipment. W. A. MUDGE

The value of molybdenum alloy steels. G. W. SARGENT. *Trans. Am. Soc. Steel Treating* **1**, 589–97(1921).—In the manuf. of Mo steel by the crucible process $CaMoO_4$ does not give as good results as Fe-Mo when the latter is added in coarse lumps instead of a fine powder. In open-hearth practice the Fe-Mo is added in the furnace immediately after the slag has been cleared up. Mo does not segregate nor cause segregation, and in addition shows uniformly higher physical values than other alloy steels. Its slightly higher cost is offset by its greater economy. Many analyses and charts showing physical properties are given. W. A. MUDGE

Studies on the working of special steels. Forging experiments with chrome-nickel construction steel. ERDMANN KOTHNY. *Stahl u. Eisen* **41**, 213(1921).—The steels for the expts. were 0.5 and 1% Cr and 4% Ni. The following conclusions summarize the results: (1) Cr-Ni steel with 0.5–1% Cr and 4% Ni should be forged from 1200° to 900°. (2) Steel with 1% Cr is more sensitive to overheating than 0.5% Cr steel. (3) By annealing the forged steel at 600° the damage done to the structure by overheating is lessened. (4) The higher the finishing temp. of forging the less accentuated is the transverse fiber. R. S. DEAN

Explain the structures of malleable. W. R. BEAN, H. W. HIGHRITER AND E. S. DAVENPORT. *Foundry* **49**, 557–64(1921).—The use of the microscope to reveal the causes of many different effects found in the fracture of malleable cast Fe is set forth. The condition of the C content is largely governed by the compn. and by the anneal. Many excellent photomicrographs are included. V. O. HOMERBERG

Breakage and heat treatment of rock drill steel. A. E. PERKINS. *Iron Age* **108**, 7–8(1921).—A study is made of the steels which give greatest service before failure by breakage. The max. and minimum service that might be expected and a comparison with eye-bars are considered. The compn. for straight C steel under the av. present-day conditions is: C 0.85–0.90, Mn 0.30–0.40, P 0.03 and S 0.03%. V. O. HOMERBERG

Occurrence of nitrogen in steel. A. A. BLUE. *Iron Age* **108**, 1–5(1921).—Needles of Fe nitride were found to be present in a drop-forged connecting rod, of light wt. design, which had been lodged in the flue of an under-fired heat-treating furnace. The temp. in the furnace proper had at no time exceeded 1600° F. These needles followed fairly consistent directions at well defined angles to each other in the same grain. Often the needles originated at the same point on the grain boundary and extended into their respective grains at different angles. The needles were occasionally found in a zigzag formation. In many instances direct openings between the grains were found. The needles completely disappeared when the specimen was heated to 1780° F. for $^1/_2$ hr. and quenched in H_2O. The specimen was then reheated to 1200° F. and allowed to cool slowly overnight in the furnace. The resulting structure showed the reappearance of traces of nitride. Reheating again in 1780° F. for $^1/_2$ hr. and cooling in the furnace resulted in the reappearance of additional nitride. Photomicrographs are included. V. O. HOMERBERG

The prevention of rust. P. MARTELL. *Neueste Erfind. u. Erfah.* **47**, 43–7 (1920); *Chimie et industrie* **5**, 328(1921).—Review of modern processes for the protection of Fe against rust. A. P.-C.

Galvanized culverts. L. G. CARMICK. *U. S. Dept. Agr., Public Roads* **3**, No. 25, 26–9(1920); *Expt. Sta. Record* **43**, 690.—Expts. on the value of the method of testing the galvanizing of metal culverts by chem. analysis of one or two small pieces cut at random from the culverts. It was found that there is a lack of uniformity in the coating on the different parts of a sheet, which may amount to as much as 50% of the av. for the sheet. This is taken to indicate that little reliance can be placed on the results from tests of one or two small pieces. In order to secure an adequate idea of the spelter coating on a shipment of culverts it is considered necessary to take quite a large number of samples. Comparative tests of the HCl–Sb chloride and the $Pb(OAc)_2$ methods of testing for spelter coating showed that when the acid method was used with 1-min. immersions the results were much too high. When the time was reduced to 30 seconds, the results were remarkably accurate, more so than those given by the acetate method. H. G.

Electric arc welding. H. M. SAYERS. *Electrician* **87**, 105(1921).—A brief review. C. G. F.

Lead corrosion with relation to sulfuric acid manufacture (MCKELLAR) **18.** Introduction and development in the United States of the use of gas producers in the zinc industry (SURNY) **21.** A colloid theory of the corrosion and passivity of iron, and of the oxidation of ferrous salts (FRIEND) **2.** Specific heats of technical copper-zinc alloys at higher temperatures (DOERINCKEL, WERNER) **2.** Blast-furnace gases (HUTCHINSON, BAINBRIDGE) **21.** The microscopic forms of iron rust (ACKERMANN) **2.** Rusting through of canned food containers of tinplate (MORGENSTERN) **12.** Carborundum refractories in heat-treating furnaces (HARTMAN) **19.** Recovering water-soluble values from furnace gases (U. S. pat. 1,377,363) **18.**

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TRILLICH, HEINRICH: **Das Rösten und die Rostwaren.** Hamburg: Verlag Wallbaum & Co. For review see *Z. öffentl. Chem.* **27**, 132(1921).

Ore flotation. B. H. DOSENBACH. U. S. 1,377,189, May 10. Ores containing a plurality of floatable constituents such as sulfides of Zn, Fe and Pb are treated in the form of a pulp with a gaseous modifying agent such as oil or tar vapor which tends to cause flotation of all of these constituents and at the same time is treated with SO_2 or other gaseous substance which has a deterent effect upon a portion only of the floatable constituents, to facilitate selective flotation.

Ore flotation. C. SPEARMAN. U. S. 1,377,937, May 10. Ore such as graphite ore is ground with an aq. soln. contg. a small amt. of oil, the material is agitated to sep. values from gang and permit particles of the values to coalesce and float on the soln. and the adhesion of the coalesced particles is then destroyed and the values are screened to sep. the larger flakes from the powdered particles.

Mineral flotation. R. E. SAYRE. U. S. 1,378,562, May 17. A small amt. of

acid-treated aldol or a similar aldehyde condensation product is used to facilitate ore sepn. by flotation. Cf. *C. A.* **15**, 1484.

Amalgamator for recovering values from ore pulps. A. C. THANE. U. S. 1,377,738, May 10.

Extracting metals. W. J. BROWNING. Brit. 162,682, July 31, 1919. A process for the extn. of metals from solns. consists in pptg. as sulfides one or more metals, such as Cu, by reaction with S and H_2S, produced by burning, calcining, or distg. a S-bearing mineral, such as pyrites, in the presence of steam. The residual gas, which contains SO_2, is reduced continuously by means of incandescent carbonaceous matter as described in 158,288, and the products, which include S and H_2S, may be used for the pptn. of metallic sulfides. Reduction is best effected when the proportion of SO_2 is 7% of the total vol. of gas.

Treating zinc ores. R. L. LLOYD. U. S. 1,378,699, May 17. Zn ore residues or other Zn-bearing material contg. but little S is mixed with coal or other reducing agent and the mixt. is heated to a temp. below that at which Zn is reduced and volatilized and is treated with a solvent to dissolve out the Zn.

Treating zinc ores. R. L. LLOYD. U. S. 1,378,822, May 17. Zn sulfide ore or similar Zn-bearing material is roasted and treated with H_2SO_4 to dissolve the Zn. The solid residue is then mixed with a reducing agent such as coal and the mixt. is heated to a temp. below the temp. at which Zn is reduced and volatilized and the remainder of the Zn is dissolved from it.

Preparing zinc ore for smelting. J. W. HEGELER. U. S. 1,378,411, May 17. A mixt. of Zn ore and C is prepd., for smelting, by mixing Zn ore with coking coal and subjecting the mixt. to a coking process.

Treating lead-zinc ores. F. E. ELMORE. Brit. 162,026, Dec. 18, 1919. Argentiferous lead-zinc sulfide ores are roasted with a halogen salt such as chloride of Na, K, Ca, or Mg in an oxidizing atm. at a temp. above 400° but not high enough to volatilize $PbCl_2$, the ZnS remaining for the most part unattacked. To prevent any appreciable attack on the Zn the temp. should not exceed 500°. The air employed in the roasting is preferably moistened if dry. The product of the roasting is leached with hot brine to extract Pb, some Ag and any $ZnCl_2$. The Pb and Ag are recovered in known manner for instance, by cooling the soln. and treating the deposited chlorides as described in 129,773 (*C. A.* **13**, 2980) to sep. the Ag as argentiferous $PbSO_4$, the brine being used repeatedly. The residual ore is treated with a solvent for Ag such as a soln. containing 35% $CaCl_2$ and 3–5% cupric chloride or 3% HCl as described in 151,698, or, if there is an appreciable quantity of Pb, the ore is first treated with hot brine containing HCl or H_2SO_4 as described in 127,641 to ext. the Pb and part of the remaining Ag, and then as above described to extract the remaining Ag. The used brine containing Na_2SO_4 and the Pb salts obtained may be treated as described in 129,773 (*C. A.* **13**, 2980) to de-sulfate the brine and obtain $PbSO_4$. In modification, if there is some unoxidized PbS remaining after the roasting or after the leaching with brine, the ore is leached with hot strong soln. of Ca or $MgCl_2$ containing enough HCl to convert the PbS into chloride. This effects a good extn. of the Ag and renders a subsequent extn. unnecessary. It is preferred to have a small quantity of $ZnCl_2$ present in the calcination; this may be derived from the ore if it contains some easily attackable Zn, or, may be added at the beginning or towards the end of the calcination, preferably as a mixt. of Na and Zn chlorides obtained by evapg. some of the brine used for leaching. Cf. 131,353, 135,968, and 141,044.

Separating nickel from nickel-copper alloys. A. MCKECHNIE. U. S. 1,377,713, May 10. Cupro-Ni alloy is melted and bessemerized in a basic converter until all

or a substantial portion of the Ni is volatilized and the fumes thus formed are collected as Ni oxide.

Separating metal values from mixtures containing tin. G. W. MULLEN. U. S. 1,377,217, May 10. White metal mat or a similar material contg. Sn is reduced with a sulfatizing material such as niter cake and coal or other reducing agent to produce sulfides of the metals present, the product is digested with H_2O to sep. sol. from insol. sulfides, the insol. sulfides are sepd. and the sol. sulfides are converted into oxides and reduced to metal.

Flame-heated crucible furnace adapted for melting metals. J. DOERSOM. U. S. 1,378,529, May 17.

Ingot-mold. O. A. FOGARTY. U. S. 1,377,962, May 10. Structural features.

Granulating slag. M. MAGUET. Brit. 162,375, Jan. 26, 1920. Basic slag is granulated by first dividing the slag as it comes from the furnace into drops, thereby cooling it to about 1300°, and thereafter projecting the drops into H_2O. The slag flows from a channel and is met by a jet of air, which may be moistened, from a pipe whereby it is projected against a hood, the inner surface of which is moistened. The drops of slag fall into a trough, through which H_2O flows and carries away the granulated product.

Granulating converter slag. S. R. GARR. U. S. 1,378,223, May 17. Converter slag as it is fed to an ore-smelting reverberatory furnace is granulated by pouring a molten charge of the slag in a stream into the furnace and projecting steam under relatively high pressure against the falling slag to disintegrate the slag and spread it over a large portion of the surface of the charge in the furnace.

Electrical treatment of hot slags to prepare fertilizers, etc. J. E. BLOOM. U. S. 1,377,554, May 10. The pat. relates to the compounding (under insulated conditions) of a molten slag as delivered from its source, with materials of other kinds which are rendered available as fertilizers by the process; *e. g.*, phosphorites or potash feldspar. The course of the reaction is controlled in part by regulation of the condition of electrification or neutralization of the materials.

Treating iron ore containing alumina. F. A. EUSTIS. U. S. 1,377,822, May 10. Fe and Al are dissolved from Cuban Fe ore or a similar ore containing both Fe and Al, by the use of a dil. soln. of H_2SO_4 or HCl and alumina is pptd. from the soln. by $CaCO_3$. The Fe is then recovered by electrolysis.

Treating iron ores. R. STÖREN and R. JOHANSON. Brit. 162,718, Dec. 29, 1919. In the treatment of poor Fe ore containing weakly magnetic or nonmagnetic O compds. of Fe by subjection to a reducing roast at about 400° to facilitate magnetic sepn., the concn. is effected while the material is still in the reducing atm. A suitable construction is given.

Iron. D. WRIGHT. Brit. 162,725, Nov. 2, 1920. Finely divided Fe ore is sprayed into an oil-fired furnace preheated to a temp. of about 1500° and worked with a reducing atm. The oil is supplied by a rotary atomizing app. or spray burner arranged in a passage and is completely burned until the requisite temp. is attained, whereupon the air supply is diminished to form a reducing atm. of CO. The ore is then sprayed into the chamber through a passage and instantaneous reduction proceeds until the temp. is reduced to about 1150°, when the chamber is again heated by an oxidizing flame. The metal and slag collect in a channel.

Iron and steel. H. LANG. Brit. 162,808, Feb. 6, 1920. See *C. A.* **14**, 1961.

Iron and steel manufacture. H. KOPPERS. Brit. 162,618, Apr. 28, 1921. In a process for desulfurizing Fe and steel as described in the German specification 67,087 vi/18 b., the Fe bath is freed from P, Mn, etc., and the slag layer is removed and replaced by a new thick layer of highly basic slag into which specially prepd. C, having

approx. the same sp. gr. of the slag, is immersed for the purpose of converting in a neutral atm. the S into CaS and at the same time remove the last traces of O in the form of CO. The C is prepd. by mixing finely ground coke with tar and forming the mixt. under great pressure into blocks provided in some cases with perforations. When required the slag bath is regenerated after the molten Fe has been removed by passing a current of air through the slag.

Steel. J. N. KILBY. Brit. 162,994, Sept. 20, 1920. A means for re-carburizing molten steel in an open-hearth furnace consists of a box which is carried on a ram and fitted with hopper-like plates to contain the carbonaceous material, and provided with an extension to pass through the slag. The extension is temporarily closed by a cover, such as a wooden plug, adapted to be melted or consumed in the molten steel. The openings between the plates and the extension are temporarily closed with paper stoppers and a vent is provided to allow the escape of gas generated during the operation.

Alloys; refining iron and steel. C. VOS. Brit. 162,917, May 5, 1920. An alloy for use in degasifying and refining molten Fe and steel is prepd. from Al-Mg, Na_2F_2, U oxide, and ferro-silicon, the final compn. of the alloy being about 90–95% of Al, 1.5–9.5% of Mg, 0.005–2.75% of U, 0.05–1.25% of ferro-silicon, and 1–1.8% of Fe.

Case-hardening iron and steel. W. H. ALLEN. U. S. 1,377,174, May 10. Selected areas of Fe or steel which are to be case-hardened are coated with shellac or similar material which may be disintegrated by heat but is insol. in aqueous slightly acid solns., the remaining areas of the metal are converted into Fe phosphates and the material is then subjected to the action of case-hardening gases.

Alloys. T. F. BRADBURY and ROLLS-ROYCE, LTD. Brit. 162,467, Feb. 25, 1920. Sb, Mg and Ti, or any two of them, are added to Cu-Al alloys containing 3–15% of Cu, or to Zn-Al alloys containing 5–20% of Zn, or to Cu-Zn-Al alloys containing 1–6% of Cu and 1–20% of Zn, the total addition being 0.5–3%, and the amt. of any one metal not exceeding 1.5%. Fe, Mn, Si, Sn, Ni, W or Cr may be present as impurities or minor constituents. In the case of an Al-Zn alloy containing Ti and Mg, the Ti does not exceed 0.8%.

Molybdenum-tungsten alloy. F. G. KEYES. U. S. 1,377,982, May 10. A bar of Mo-W alloy is formed by molding the moistened metals, drying, heating to about 1200° and treating with a slow stream of dry H.

Making tungsten wire. PATENT-TREUHAND-GES. FÜR ELEKTRISCHE GLÜHLAMPEN. Brit. 163,014, May 6, 1921. In making tungsten wire, particularly for elec.-lamp filaments, a blank consisting of rods which contain or are bound together to produce in their cross-section zones differing from one another as regards their compn. in physical properties, is drawn and then submitted to a heat treatment so that the crystals form uniformly along the length of the wire. The length of the crystals in the direction of the axis of the wire exceeds the diam. of the wire several times. The blank may differ in compn. from the axis to the circumference or from side to side, or may contain different sectors. The blank may consist of a casing into which circular, rectangular or other structures of desired compn. are inserted, the casing or core consisting of pure W, W and ThO_2, or W alloyed with metals or metalloids such as Mo, Th, Ta, V, Cr, C, or P or mixts. or compds. thereof or with other elements dissolved or admixed therewith. Examples are cited.

Tungsten-zirconium alloys; electric filaments. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 162,907; Apr. 19, 1920. A W alloy, particularly for elec.-lamp filaments, is made by sintering together Zr intimately mixed with W with which is incorporated, by the method described in 155,851 (*C. A.* **15**, 1661), a small % of SiO_2 or equiv. material. A combination of W and Zr may be prepd. by reduction of a mixt. of compds. of Zr and W; a quantity of tungstic acid mixed with the SiO_2, etc., is added before

final reduction, pressing, and sintering. The Zr may be prepd. by reducing ZrO_2 with Mg.

Magnesium-manganese alloy. W. R. VEAZEY. U. S. 1,377,374, May 10. An alloy, which gives castings of high strength, formed of Mg 99.5–92 and Mn 0.5–8% is prepd. by adding $MnCl_2$ to molten Mg and flux.

Coating steel sheets with aluminium. S. PEACOCK. U. S. 1,378,052, May 17. Steel sheets are coated with Al by first passing them through molten double chloride of Al and Na and then through molten Al. A firmly adhering coating is thus formed.

Coating ferrous metals with antimony and lead. C. BASKERVILLE. U. S. 1,378,439, May 17. Fe or steel is coated with Sb or Pb-Sb alloy and then with an overlying layer of Pb. The Sb serves to unite the Fe and Pb to form a durable non-rusting surface.

Electric welding apparatus. H. R. PENNINGTON. U. S. 1,378,192, May 17.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

Photocatalysis. I. The synthesis of formaldehyde and carbohydrates from carbon dioxide and water. EDWARD C. C. BALY, ISIDOR M. HEILBRON AND WILLIAM F. BARKER. Univ. Liverpool. *J. Chem. Soc.* 119, 1025–35(1921).—An aq. soln. of CO_2 gives HCHO when exposed to light of very short wave length ($\lambda = 200\ \mu\mu$). An aq. soln. of HCHO is polymerized to reducing sugars in light of wave length 290 $\mu\mu$. In the presence of paraldehyde, PhONa and certain metallic salts which absorb light of wave length 290 $\mu\mu$, the yield of HCHO is materially increased. These substances do not catalyze the reaction but protect the HCHO, when formed, from polymerization. The photosynthesis of HCHO from CO_2 and H_2O can be photocatalyzed by certain colored basic substances, *e. g.*, colloidal U hydroxide and $Fe(OH)_3$, malachite green, Me orange, etc. The photosynthesis then takes place in visible light. The polymerization of HCHO to give carbohydrates has also been photocatalyzed. When carbohydrates, $C_3H_5(OH)_3$, Me_2CO, $C_2H_2O_4$, etc. are exposed in H_2O to the light from the quartz Hg lamp, HCHO and reducing sugars are formed. An equil. is set up between sugar, HCHO, and CO_2. When exposed to the unscreened light from the Hg lamp, this equil. apparently lies far over to the side of the CO_2. By the action of light from the Hg lamp on a concd. soln. of K_2CO_3, considerable quantities of HCHO are produced, but insufficient to give a positive test for sugar. If, however, more pure HCHO is added, a positive test for reducing sugar will be obtained after a further exposure of a few hrs. In the presence of a photocatalyst capable of catalyzing both stages of the reaction, this equil. will be shifted entirely over to the side of the reducing sugar. Chlorophyll would seem to be an ideal photocatalyst for both stages of carbohydrate synthesis from CO_2 and H_2O. The formation of carbohydrates in the growing leaf from a very small concn. of CO_2 without the free existence of HCHO as an intermediate product is thus explained.

C. J. W.

Some transformations of trioxymethylene. A. CONTARDI. R. Scuola Sup. di Agri., Milan. *Gazz. chim. ital.* 51, I, 109–25(1921).—For some time C. has been occupied with the org. compd. present in seeds as a Ca and Mg salt (*C. A.* 4, 1619, 2454). This compd. according to Posternack (*Rev. gén. botanique* 12, (1900)) is the result of a special transformation of HCHO with sol. acid phosphates, giving rise to anhydrohydroxymethylenediphosphoric acid, $O[CH_2OP(:O)(OH)_2]_2$, 3 mols. of which by the addition of 3 mols. H_2O and the loss of 3 H_3PO_4 give rise to inositol. According to this view HCHO is present as $H_2C(OH)_2$ in aq. soln. of which 2 or more mols. may give compds. like $HOCH_2OCH_2OH$ by the loss of H_2O. The latter in turn by reacting with H_3PO_4

on the terminal OH groups may give phosphoric esters. C. studied the action of concd. H_3PO_4 on HCHO (*C. A.* **7**, 1870) and obtained $H_2C[OP(:O)(OH)_2]_2$ (A) as a highly stable compd. 15 g. dry resublimed trioxymethylene (B) and 98 g. H_3PO_4 free from H_2O heated in a sealed tube for 10 hrs. at 140–5° gave a straw-colored sirup of A; this was dried at 110°. In prepg. A on a larger scale excess of B was heated in a beaker in an autoclave at 140–50°. In this process the antiseptic and antifermentative properties of HCHO disappear. The K salts of A may be used in the EtOH fermentation of sugar in place of the K_2HPO_4. The Ca and Ba salts of A are little sol. in cold H_2O and less so in warm H_2O. When heated to 400° they lose HCHO quant., giving the corresponding pyrophosphate with no appreciable charring. These salts are richer in P than any org. phosphates known and because of their behavior on heating would be difficult to recognize in the juice of a plant, where they might easily be confused with acid phosphates. With HNO_3 A does not give Scherr's reaction but on electrolytic oxidation of A, as with inositol, the org. part is oxidized to CO_2. AcH, EtCHO and PrCHO are tarred when treated with H_3PO_4 under the conditions that gave A. Most of the aromatic aldehydes do not react with H_3PO_4. Me_2CO treated with H_3PO_4 at 150° gives $Me_2C{:}CHAc$, b. 130°, and phorone, b. 198°. All of the well known work on the polymerization of HCHO with alkalies, dil. acids or metallic Zn gave sugar-like substances but in no case cyclic compds. If such compds. are obtainable the conditions of polymerization must be different. In 1888 Berthelot studied the fixation of N_2 in plants by subjecting paraldehyde+N_2 to silent electric discharge. C. repeated these expts., using 1 kg. dry HCHO in the form of B at 140–5° in 20 glass tubes for 50 hrs. At the end some CO_2 was found and a liquid, d_{14} 1.133, containing 14.14% acid calcd. as HCO_2H. On fractionation HCO_2Me, b. 22°, $HCH(OMe)_2$, d_{14} 0.856, b. 42°, and a 3rd liquid, b. 100°, composed of a H_2O soln. of HCO_2H, HCHO and its sol. polymers, were obtained. 51% of the B used was recovered unchanged. In general the results showed that the silent discharge is without action on gaseous HCHO. Heated at 140° HCHO is capable of giving sugar-like substances in the absence of H_2O but even in these conditions HCHO is not polymerized to give inositol. C. reviews the existing work on the electrolytic oxidation of polyhydric alcs. and similar compds., especially that of Löb (*C. A.* **3**, 1876) and then describes similar expts. with inositol and phytin designed to det. whether HCHO is formed, as is so frequently the case with the other compds. mentioned. 50 g. inositol in 250 cc. 20% H_2SO_4 was subjected to electrolytic oxidation in an app., which is described, having 2 Pt electrodes 5 cm. sq., at 7.5 amps. per sq. cm. for 150 hrs. The H_2SO_4 was removed with $Ba(OH)_2$ and the filtrate evapd. to dryness *in vacuo*. The solid residue was extd. with EtOH and Et_2O and gave a product that decomps. 160°, evolving gas and giving a black residue. This substance gave the tests of leuconic acid and was converted into croconic and hydrocroconic acids. Some $(CO_2H)_2$ but no HCHO was obtained. The $(CO_2H)_2$ arises from the oxidation of leuconic acid, as was shown by test expts. Inositolhexaphosphoric acid similarly oxidized gave leuconic acid, a little $(CO_2H)_2$ but no HCHO. Earlier work on the oxidation of inositol with HNO_3 is reviewed and especially that of Maquenne, who obtained tetrahydroquinone (C), rodizonic acid (D), triquinoyl (E) and croconic acid (F). Of these E is unstable, m. 95°, and on oxidation gives E and CO_2. F on oxidation gives leuconic acid. 50 g. powdered inositol when heated with 150 cc. HNO_3 (d. 1.7) evolved much N oxides and CO_2. The product on evapg. to dryness was found to be pure leuconic acid. No $(CO_2H)_2$ nor HCHO was obtained. The above represents an easy way for prepg. leuconic acid from inositol. The prepn. of inositol from phytin was simplified as follows: the powdered phytin is mixed to form a paste with 60% H_2SO_4 and heated in a porcelain beaker in an oil bath at 160° for 15 hrs. After cooling the mixt. was poured into H_2O, neutralized partly with $Ca(OH)_2$

and made alk. with $Ba(OH)_2$. The excess $Ba(OH)_2$ was carefully removed from the filtrate with H_2SO_4 and from the soln. on evapn. inositol crysts. Phytin and both natural and synthetic inositolhexaphosphoric acid all behave similarly on oxidation with HNO_3. Other work on the significance of inositol in the organism is under way. Also in *Atti accad. Lincei* 29, II, 321–4(1920). E. J. WITZEMANN

Action of 2,3-dibromopropylene on magnesium isopropyl bromide. LESPIEAU. *Compt. rend.* 172, 1236–8(1921).—Lespieau and Bourguel (*Compt. rend.* 170, 1584 (1920)) have already described the prepn. of acetylenic hydrocarbons by the action of CH_2:$CBrCH_2Br$ (A) on the organomagnesium derivs. With the object of generalizing the method, it has been applied to the Mg derivs. of a sec. bromide, *viz.*, iso-PrMgBr (B). The action of A on B is so energetic that it must be carried out in the presence of a large quantity of Et_2O, A being added until further additions no longer produce heat. The soln. is then treated with acidulated H_2O, extd. with Et_2O and the solvent evapd. Fractional distn. yields iso-BuCBr:CH_2 (C), colorless liquid, b. 126–7°, d 1.207, n_D^{18} 1.4627, $M._D$, calcd. from the latter, 37.17; mol. wt. in freezing AcOH, 168; Br content, 49.21%. The yield of C based on the amt. of A used is only ca. 30%. Simultaneously, violet liquids are formed which are decolorized on shaking with K_2CO_3 soln. and from which it is difficult to isolate a definite compd. By means of numerous distns. under reduced pressure, however, a colorless liquid was sepd. b_{11} 63°, d_{24} 1.0942, n_D^{24} 1.456, mol. wt. detd. as for C, 215, Br 38.10%. These values indicate that the compd. may be a *bromononane* resulting from the fixation of B on the double bond of A, probably in such a manner as to give iso-BuCMe(CHMe$_2$)Br. Starting with C several other compds. were synthesized in the manner indicated below. The mol. wt. given was in all cases detd. by the f. p. method using AcOH. The *isohexyl tribromide*, iso-$BuCBr_2CH_2Br$ (D), was prepd. by adding 2 atoms of Br to C, b_{16} 116–7°, d_{17} 1.986, n_D^{17} 1.561, mol. wt. 339, Br 74.23%. D by the action of EtONa gave good yields of iso-BuCBr:CHBr (E), b_{11} 70–1°, d_{17} 1.621, n_D^{17} 1.512, mol. wt. 248, Br 66.52%. E warmed moderately for several hrs. with Zn powder and 95% alc., distd. and rectified by means of a Dufton column gave 2 fractions (*a*) b. 54.5–5.0° and (*b*) b. 78°; (*a*) proved to be a const. boiling mixt. of the alc. used and the acetylenic hydrocarbon, iso-BuC : CH (F). To isolate F the mixt. was left several days in contact with fused $CaCl_2$, the liquid decanted and distd. F is a very volatile liquid with a strong alliaceous odor, b. 61.5–2.0°, d_0 0.7244, mol. wt. 82, C and H, resp. 87.50% and 12.28%; it reacts with NH_3-Cu_2Cl_2 and ppts. alc. $AgNO_3$, forming iso-BuC : CAg.$AgNO_3$, brilliant plates, sol. in hot alc.

A. T. FRASCATI

Oxidation of acetoacetic acid. N. O. ENGFELDT. *Z. physiol. Chem.* 112, 176–86 (1921); *J. Chem. Soc.* 120, I, 158.—On adding $KMnO_4$ to Na acetoacetate a vigorous reaction follows and acetic, oxalic, and glyoxylic acid are formed. It is assumed that at a certain stage of the oxidation process the acetoacetic mol. is broken up, with the production of AcOH and glyoxylic acid, the latter acid being eventually oxidized to $(CO_2H)_2$. Hydroxybutyric acid does not react vigorously with $KMnO_4$, at the ordinary temp., but at the boiling temp. acetone and CO_2 are formed if the reaction of the liquid is strongly acid; $(CO_2H)_2$ and AcOH are produced when the reaction is weakly alk. or neutral. It is assumed that acetoacetic acid is formed as an intermediate product in the oxidation of the hydroxybutyric acid. H. V. ATKINSON

Applications of the chemistry of complexes to problems of organic chemistry. I. A new method for the titration of enols in keto-enol mixtures. WALTER HIEBER. Univ. Würzburg. *Ber.* 54B, 902–12(1921).—The Meyer Br method, in spite of the services which it has rendered, does not always fulfil the two essential requirements of an analytical detn. of an equil. mixt., *viz.*, that the enol form alone should react instantaneously and that the reagent should exert no appreciable catalytic influence on

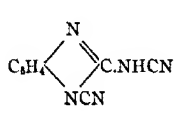
the rearrangement of the desmotropes. H. proposes a new method based on a reaction, not with the double bond but with the OH group, *i. e.*, on the ability of enols to form with $Cu(OAc)_2$ salts almost or wholly insol. in H_2O but easily sol. in org. solvents. The substance is quickly dissolved in alc., treated with $Cu(OAc)_2$ in EtOH-$CHCl_3$, the enol salt at once sepd. in $CHCl_3$ soln. by adding H_2O, decompd. with dil. H_2SO_4 and, after removal of the $CHCl_3$, analyzed iodometrically for Cu. Under the proper exptl. conditions, the enols react instantly with $Cu(OAc)_2$ and the excess of $Cu(OAc)_2$ does not appreciably shift the equil. point or accelerate its establishment. The influence of temp. and length of reaction is much less pronounced than in the Br method. To carry out a detn. the necessary amt. (6–10 cc., see below) of $Cu(OAc)_2$ soln. (50 g. $Cu(OAc)_2$.-H_2O in 1 l. H_2O), 12 cc. alc. and 6–8 cc. $CHCl_3$ at $-10°$ is added to the quickly prepd. soln. of the mixt. of desmotropes in a little cold alc. (+$CHCl_3$, if necessary), shaken, at once, poured into about 250 cc. H_2O in a separatory funnel (this requires 5–10 sec.), shaken a few times, the $CHCl_3$ soln. run into a second funnel, decompd. with dil. H_2SO_4, freed from the $CHCl_3$, treated with 2–3 g. KI and titrated with 0.1 *N* $Na_2S_2O_3$ and starch. The whole detn. can easily be carried out in 5–10 min. The reaction between the enol and $Cu(OAc)_2$ occurs only before the sepn. of the $CHCl_3$ enol salt and the aq. $Cu(OAc)_2$ solns.; when this has taken place there is no measurable reaction between any enol subsequently regenerated in the $CHCl_3$ and the Cu in the aq. soln. so that the funnel can be rotated to effect a very exact sepn. and the last traces of the enol salt soln. remaining in the first funnel can be rinsed out with $CHCl_3$. Preliminary expts. showed that no $Cu(OAc)_2$ is extd. from aq. soln. by $CHCl_3$, even in the presence of alc., and conversely, that no enol salt remains in the aq. layer after shaking with $CHCl_3$; also, in the case of desmotropes which cryst. in homogeneous form (Me mesityloxide-oxalate and benzoylacetone) that the $Cu(OAc)_2$ acts instantaneously and completely with the enol. In applying the method to mixts. of desmotropes the amt. of $Cu(OAc)_2$ (to be detd. by preliminary titration) must be so chosen that it is about twice that required to combine with the enol. The following results were obtained (the values obtained by the Br method are given in parentheses) with the method: Benzoylacetone at equil. in abs. alc. at $-8°$, 4.6% ketone (6%). Acetoacetic ester in alc. at $-8°$ directly after dissolving, 7.44% enol (7.51%) (if the solvent is used at temps. ranging from $-8°$ to 50°, the results vary only within the limits 7.36–7.74%, and if the time elapsing between the mixing and the pouring into the H_2O is varied from 5 sec. to 20 min., the % of enol found increases only from 7.43 to 8.57). Acetoacetic ester at equil. in alc., 12.23% enol (12.5%). The following detns. (% enol) were made at 16°: acetylacetone, 76.38 (76.5); methylacetylacetone, 30.8 (31.21); Et ethylacetoacetate, 2.98 (3.00); Me acetoacetate, 4.74 (4.8); Et benzoylacetate, 29.3 (29.2); oxalacetone, 71.26–71.58 (140–70); oxalacetic ester, 52.12–52.27 (80–8). Thus, while acetoacetic ester and analogous compds. yield concordant results by both methods, in the case of the oxalylketones, in which different complications occur in the Br method, the new method yields considerably lower results. The Cu method could not be applied to acetyldibenzoylmethane, as the enol salt proved to be insol. in $CHCl_3$.

CHAS. A. ROUILLER

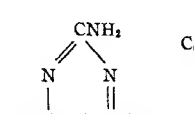
The action of light on the acetone and alcohol solutions of chloropicrin. A. PIUTTI. Univ. Naples. *Gazz. chim. ital.* **51, I,** 145–6(1921).—Freshly distd. chloropicrin (A) is a colorless liquid b_{752} 111.91°, d_0 1.69247, which becomes yellow in diffuse light and in sunlight assumes the color of nitrous vapors. The solns. of A in EtOH, MeOH, C_6H_6, turpentine, AcOH, etc., remain unchanged in the dark but exposed to light they all become colored except those in alcs. The solns. in alcs. after 1 day sep. into 2 layers and white crystals of NH_4Cl sep. at the bottom. Me_2CO solns. are somewhat colored, do not sep. in 2 layers but deposit NH_4Cl also. Evidently the alcs. reduce the NO_2

to NH_2 and then NH_3. Reductions by alc. in light were observed by Ciamician and Silber (*Gazz. chim. ital.* **26**, 111(1886)) and others but this instance is striking because the NH_2 is reduced only in the light. The alc. or Me_2CO soln. may be boiled in the dark and remains unchanged. Some data from the literature on the reduction of A with $SnCl_2$, HCl and nascent H_2 are reviewed. The products of the reaction here described are to be detd. by further work. E. J. WITZEMANN

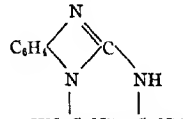
The action of cyanogen halides upon phenylhydrazine. V. Derivatives of melamine. G. PELLIZZARI. R. Ist. Sup., Florence. *Gazz. chim. ital.* **51**, I, 89–107(1921).—In a preceding paper (*Gazz. chim. ital.* **37**, II, 611) it was shown that $PhNHNH_2$ in H_2O with cyanogen halides gives *o*-phenylene-α,β-dicyanoguanidine (I) which acts like an acid. In NaOH or KOH, I loses a CN group, giving *o*-phenylene-β-cyanoguanidine which in HCl loses an-



I

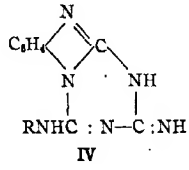


II

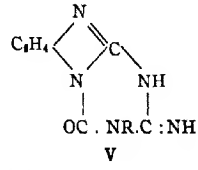


III

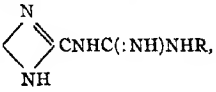
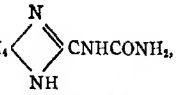
other CN group, giving *o*-phenyleneguanidine. In NH_4OH instead I gives a basic addiion product with 1 NH_3. I gives similar products with $PhNH_2$ and $PhNHNH_2$. These products through their properties and behavior may be considered as derivs. of melamine (II) (or its imidic isomer) having the constitution III (or one of its possible isomers). It is less probable that the N of the base added enters the ring, forming the melamine nucleus giving IV or its isomers. The compd IV or its isomer was obtained in another way by P. as will be shown in another paper and is not identical with these products. II, as is known, boiled with acids or with bases is sapond. to ammeline, melanuric and cyanuric acids. III undergoes a similar transformation in part, giving the corresponding isoammeline (V), for which the intermediate melanuric acid was not isolated. With

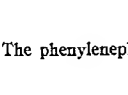


IV

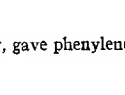


V

NaOH or KOH, instead of the melanuric acid, V easily gives by ring rupture CO_2 and the phenylenebi guanide (A),  of KOH gives the phenyleneguanylurea (B),  finally by sapon. the phenyleneguanidine. B is identical with the same compd. previously obtained (Paper IV) and this establishes the constitution of A. If the CO group were on the opposite side of the ring in formula V the products would have corresponded to phenylene-α-guanylurea (*C. A.* **14**, 169). A was previously prepd. by Ziegelbauer (*Monatsh.* **17**, 653) from *o*-$C_6H_4(NH_2)_2$ and dicyanodiamide but he wrongly

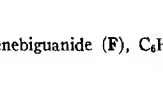
assigned the sym. formula to it. The phenylenephenylbiguanide (C), 

NHC(:NH)NHPh, which was similarly obtained from phenylenephenylmelamine by converting it first into phenylenephenylisoammeline, does not give the corresponding guanylurea but decomps. profoundly, giving CO_2, NH_3, $PhNH_2$ and phenylene-

guanidine. C with HNO_2, however, gave phenyleneguanylphenylurea, 

NHCONHPh. The corresponding derivs. of $PhNHNH_2$ were obtained and retain the NNH_2 group which reacts with aldehydes, giving condensation products. 20 g. crude I (*C. A.* **13**, 1584) suspended in 200 cc. H_2O was dissolved on adding excess NH_4OH (a red impurity was removed by filtering) and on the H_2O bath for an hr. gave 21 g. of a white microcryst. ppt. of *o-phenyleneisomelamine* (III), does not m. up to 300°. 10 g. III were boiled over a free flame with 125 cc. H_2O+50 cc. fuming HCl and on cooling sepd. 11 g. of *o-phenyleneisoammeline hydrochloride* as minute heavy needles having no m. p. The *free base* (D) (R=H in V) was obtained on adding a little excess NH_4OH and seps. as a white cryst. crust having no m. p. The *potassium salt* of this base is a colloidal gel which is easily dissolved on warming or dilg. 10 g. III or D suspended in 100 cc. H_2O+40 cc. 20% KOH and boiled for 4 hrs. under a condenser sepd. about 5 g. *o-phenylenebiguanide* (E), which was purified with animal C in H_2O and sepd. as pearly leaves, decomp. about 245°. The E of Ziegelbauer was prepd. (m. 242°), also the acid nitrate $(C_8H_9N_5)_2.5HNO_3.3H_2O$, m. 178° or 160° if heated slowly. The *neutral nitrate* of E, $C_8H_9N_5.HNO_3$, was obtained by dissolving the calcd. amt. of E in the soln. of the acid nitrate, white needles, m. 216° (decompn.). The *chloroplatinate* of E, $(C_8H_9N_5.HCl)_2PtCl_4$, was obtained by dissolving the base in H_2O with HCl so that it remained in soln. in the cold and then adding $PtCl_4$, as orange needles. The *picrate* of E, $C_8H_9N_5.C_6H_2(NO_2)_3OH$, seps. as long yellow needles, m. 269–70°. 4.5 g. E boiled under a condenser in 30 cc. H_2O+15 cc. 20% KOH for 2.5 hrs. and then concd. gave 0.55 g. unchanged E and the soln. on treatment with CO_2 and concg. gave 0.6 g. B. 10 g. pure I (obtained by dissolving crude I in NH_4OH and pptg. with HCl) suspended in 400 cc. EtOH with 10 g. $PhNH_2$ and boiled under a condenser for 1 hr. was slowly dissolved and on cooling sepd. 12.5 g. *o-phenylenephenylisomelamine* (F) as fine white needles with 1 H_2O, m. 241°; *chloroplatinate*, $(C_{15}H_{12}N_6.HCl)_2PtCl_4$, bright yellow crystals. 10 g. F boiled with 50 cc. H_2O+25 cc. concd. HCl sepd. 10 g. of *o-phenylenephenylisoammeline hydrochloride* as heavy colorless crystals. The *free base* (G) sepd. with NH_4OH forms colorless needles with 1 H_2O, m. 292° (decompn.). The *nitrate* of G, $C_{15}H_{11}N_6O.HNO_3$, seps. as minute white crystals, m. 225° (decompn.), leaving a black residue. 5 g. G in 50 cc. H_2O+50 cc. 20% NaOH boiled under a condenser 0.5 hr. was modified but not dissolved, giving *o-phenylenephenylbiguanide* (H), fine white needles from EtOH, m. 178°. The *nitrate* of H, $C_{14}H_{13}N_6.HNO_3$, seps. as a heavy powder, m. 173–4° (decompn.); crystd. from H_2O the *neutral nitrate* of H, m. 95°, is obtained as white needles. The *chloroplatinate* of H seps. as orange-yellow crystals. 5 g. H were dissolved slowly on warming with 300 cc. H_2O+5 cc. concd. HCl and the tepid soln. was treated with 1 g. KNO_2. The green-yellow liquid evolved N and sepd. 4.2 g. of *o-phenyleneguanylphenylurea hydrochloride* as a slightly yellow powder, m. 193°. The *free base* was sepd. with NH_4OH and purified from EtOH as minute shining crystals, decomp. about 250°, losing $PhNH_2$. 5 g. I were suspended in 100 cc. H_2O and 2.5 cc. $NH_2NH_2.H_2O$ were added. The reaction was completed by heating 0.25 hr. on the H_2O-bath and

6 g. of *o-phenyleneaminoisomelamine* (J) sepd., shining colorless needles with 1 H_2O, decomp. 283°. The ease of reaction of bases with I increases as the strength of the base used in these reactions. 4 g. J boiled with 60 cc. H_2O+20 cc. concd. HCl for 0.5 hr. sepd. on cooling 4 g. of *o-phenyleneaminoisoammeline hydrochloride* (K) as shining needles with 1 H_2O, becomes opaque about 150°, m. 289°. The *free base* of K was pptd. with Na_2CO_3 as white microneedles, m. 303°. K in H_2O containing HCl treated with BzH gave *benzylidenephenyleneaminoisoammeline hydrochloride* (L) as fine needles, decomp. on heating to det. the m. p. The *free base* of L seps. as fine needles that do not m. 300°. 2.5 g. of the base boiled 0.5 hr. with 50 cc. H_2O+25 cc. 20% NaOH is changed but not dissolved but on adding 75 cc. H_2O dissolves. On cooling *o-phenyleneaminobiguanide* seps., nearly colorless crystals from EtOH, m. 195–7°, alk. to litmus. E. J. W.

Synthesis of o-phenyleneguanidine from o-phenylenediamine. G. PELLIZZARI. R. Ist. Sup., Florence. *Gazz. chim. ital.* **51**, I, 140–44(1921); *Atti accad. Lincei* **30**, I, 39–44(1921); cf. preceding abstr.—In a preceding paper (P. and Gaiter, *C. A.* **13**, 1584), it was found that CNBr acting on $PhNHNH_2$ gives *o*-phenylene-α,β-dicyanoguanidine (A), which on hydrolysis with KOH and then HCl gives *o*-phenylene-β-cyanoguanidine (B), phenyleneguanylurea (C), and phenyleneguanidine (D). Pierron (*Ann. chim. phys.* [8] **15**, 190) synthesized D from *o*-$C_6H_4(NH_2)_2$ and CNBr and this on further treatment with CnBr (P. and G. *l. c.*) gave *o*-phenylene-α-cyanoguanidine (E) instead of B. The K salt of E with CNBr gave A, however. P. has now obtained B from *o*-$C_6H_4(NH_2)_2$ by first prepg. phenylenebiguanide (F),  CNH-C(:NH)NH_2, which does not have the constitution assigned to it by Zieglebauer for reasons previously given (cf. preceding abstr.) and clearly reviewed here. 10 g. *o*-$C_6H_4(NH_2)_2.2HCl$+10 g. dicyanodiamide in 100 cc. H_2O were boiled under a condenser 5–6 hrs. On adding excess NaOH 6.5 g. F sepd., pearly plates, m. 254°. 5 g. F in 100 cc. H_2O treated with 10 cc. concd. HCl and about 2.5 g. KNO_2 and left in the cold became yellow, evolved N_2 and on adding 1.25 g. more KNO_2 sepd. 3.9 g. of B identical with that previously obtained. This represents a new reaction of HNO_2 in which a RNHC(:NH)NH_2 group is converted into RNHCN instead of a urea group. The synthesis of A may then be accomplished thus: *o*-$C_6H_4(NH_2)_2 \rightarrow F \rightarrow B \rightarrow A$. E. J. W.

Conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. II. Products derived from α-halogenated adipic acids. CHRISTOPHER KELK INGOLD. Imperial Coll. Sci. Techn., South Kensington. *J. Chem. Soc.* **119**, 951–70(1921); cf. *C. A.* **15**, 1696.—One essential step in testing the hypothesis proposed in the 1st article is to test the relative ease of formation of cyclopropane and cyclobutane rings. With halogenated glutaric acids, aq. alkali gave the HO deriv., while alc. alkali gave 50% cyclopropanedicarboxylic acid. With the adipic acids, both reactions gave the HO deriv., only about 1% of the cyclic deriv. being formed. This indicates the great difficulty with which the formation of a cyclobutane ring is attended as compared with the cyclopropane ring. Adipic acid was prepd. by oxidizing cyclohexanol with HNO_3. *Ethyl α-chloroadipate*, $C_{10}H_{17}O_4Cl$, was prepd. by warming a mixt. of 500 g. adipic acid and 1000 g. $SOCl_2$ until no more SO_2 was evolved, adding 10 g. I, and passing a rapid stream of Cl at 80° until the calcd. gain in wt. occurred, and then pouring into alc., b_{18} 129–31°. *α-Bromo derivative*, b_{18} 161–3°. 2 *N* Na_2CO_3 gave only the HO deriv. 6 *N* KOH in MeOH with the Cl ester gave 7.2% Δ^{α}-dihydromucic acid, 0.9% *cis*-cyclobutane-1,2-dicarboxylic acid (Perkins, *J. Chem. Soc.* **65**, 582) and 59% HO deriv. The Br deriv. gave practically the same result. The di-Br ester, m. 66° (*Ber.* **35**, 2066) is Et *meso*-α,δ-dibromoadipate.

since it gives the *meso*-dibromo acid on hydrolysis (*Ber.* **37**, 2091). The oily residue is almost pure *racemic ester*, $C_{10}H_{16}O_4Br_2$, crystd. from EtOH at −30°, m. 9.5°, the constitution of which was established by changing it into *trans*-tetrahydrofuran-2,5-dicarboxylic acid (*J. Chem. Soc.* **77**, 115). On standing at room temp. the racemic ester changes slowly into the *meso*-form, the m. p. being depressed to the extent of 2–4° every week. When distd. *in vacuo* 30% *meso*-form is produced. In addition to the racemic ester, *ethyl α,α-dibromoadipate* is also found in the oily ester, and is purified by distn. and crystn., $b_{10\text{-}5}$ 192–3°. The constitution was detd. by hydrolysis to α-ketoadipic acid. When either ester is boiled with alc. NaI, a mixt. of I derivs. is formed. *Ethyl meso-α,δ-diiodoadipate*, $C_{10}H_{16}O_4I_2$, sepd, by crystg. from 95% alc., dense needles, m. 92% *meso-acid*, $C_6H_8O_4I_2$, minute needles from AcOH, m. 213°. The 2nd ester was the *dl-α,δ-diiodoadipate*, clusters of fine needles from petr. ether, m. 46°. *dl-α,δ-Diiodoadipic acid*, crystd. from HCO_2H, m. 170°. The *dl-iodo ester* was less readily converted into the *meso*-form than the corresponding Br ester. Treated with 2 *N* Na_2CO_3, these esters gave principally the corresponding di-HO acids. Concd. MeOH-KOH gave a mixt. of 6 acids in the following yields (the figures are for the *meso*- and *dl*-Br esters and *meso*- and *dl*-I esters): *meso*-dihydroxyadipic acid, 16, 5, 23, 2; *dl*-dihydroxyadipic acid, 9, 7, 14, 3: *cis*-tetrahydrofurandicarboxylic acid, 13, 7, 23, 2; *trans*-tetrahydrofurandicarboxylic acid, 0, 10, 0, 4; muconic acid, 55, 60, 33, 78; cyclobutene-1,2-dicarboxylic acid, 0, 2, 0, 4. The main point of interest here is the small amt. of the cyclobutene acid, since in the expt. with the corresponding glutarate deriv., 90% of the material became involved in ring formation. The sepn. was carried out as follows: 360 g. di-Br ester were heated to 100° and poured in a thin stream into 1800 cc. of boiling 6 *N* KOH in MeOH. The insol. K salts consisted of K muconate and KCl. These were decompd. with HCl and washed with H_2O. The MeOH soln. was dild. with a large vol. of EtOH and the K salt filtered. The filtrates were concd., esterified, distd., boiled with KOH-EtOH, and the K salts crystd. and added to the ppt., above. With the *meso*-esters the product is *cis*-tetrahydrofuran-2,5-dicarboxylic acid, while if the *dl*-ester is used, there results a mixt. of the *trans*-acid, together with Δ^1-cyclobutene-1,2-dicarboxylic acid, isolated as the Me ester. The more sol. portions consisted of the dihydroxyadipic acids. The constitution of these esters is discussed. Incidentally, this method is a good one for the prepn. of large amts. of muconic acid. C. J. West

α-Monosodium glyceroxide. Its structure and application. Arthur Fairbourne and Harold Toms. Univ. London. *J. Chem. Soc.* **119**, 1035–1040(1921).—*α-Monosodium glyceroxide*, $HOCH_2CH(OH)CH_2ONa$ (A), by adding slightly less than 1 mol. $C_3H_5(OH)_3$ to 23 g. Na in 350 cc. abs. alc., seps. with 1 EtOH, which is removed by heating 5 hrs. at 100° and 25 mm. 11.4 g. A and 20.25 g. 2,4-$(O_2N)_2C_6H_3Cl$ dissolved in 104 and 206 cc. $C_3H_5(OH)_3$, resp., cooled to 100° and mixed, then heated almost to boiling for 20 min. and poured into 1180 cc. H_2O, gave 90% of *glycerol α-2,4-dinitrophenyl ether* (B), $(O_2N)_2C_6H_3OCH_2CH(OH)CH_2OH$, m. 85° (Willgerodt, *Ber.* **12**, 769, gives 83°). The alk. soln. is deep red, but acid gives a colorless soln. *Diacetate*, $C_{13}H_{14}O_9N_2$, m. 106–7°. Attempts to oxidize $(O_2N)_2C_6H_3OCH_2CH{:}CH_2$ failed. *2, 4-Dinitrophenyl β,α-dibromopropyl ether*, $C_9H_8O_5N_2Br$ (C), by adding Br to the allyl ether in $CHCl_3$, small hard plates with silvery luster, m. 110°. The action of AcOAg on (B) in AcOH gave the diacetate described above, thus establishing its constitution. The action of PBr_3 on B gave C, which is a confirming proof. This paves the way for the prepn. of monosubstituted derivs. of C_6H_5OH of known constitution. C. J. West

The preparation and properties of some salts of uric acid. L. J. Curtman and D. Hart. College City N. Y. and Harriman Research Lab. *J. Biol. Chem.* **46**, 599–613(1921).—*Zinc urate*, $ZnC_5H_2N_4O_3.2H_2O$, obtained as a white flocculent ppt. by the addition of aq. $(AcO)_2Zn$ to aq. mono-K urate or to uric acid in C_5H_5N or glycerol,

insol. in H_2O, EtOH, MeOH, Et_2O, Me_2CO, AcOH, somewhat sol. in HCl, dil. HNO_3, NaOH, NH_4OH and in a mixt. of NH_4Cl and NH_4OH, completely sol. in concd. H_2SO_4 and in concd. HNO_3 with copious evolution of NO_2. *Nickel urates:* double salt $NiC_5H_2N_4O_3.NiCO_3.2H_2O$, from a mixt. of mono-K urate and an insufficient amt. of $(AcO)_2Ni$ rendered just alk. with K_2CO_3 and agglutinated by AcOK; $Ni(C_5H_3N_4O_3)_2.xH_2O$, the amt. of H_2O depending on the extent of drying, from mono-K urate and excess of $(AcO)_2Ni$ soln., insol. in the same solvents as Zn urate, decompd. by dil. or concd. HCl or dil. H_2SO_4, giving a white ppt. of uric acid, dissolves in concd. H_2SO_4 and in concd. HNO_3, giving a green soln. and copious fumes of NO_2. *Copper urates:* $7CuC_5H_2N_4O_3.3CuO.4H_2O$, from mono-K urate and $(AcO)_2Cu$ solns. or uric acid in C_5H_5N and $(AcO)_2Cu$; $5Cu(C_5H_3N_4O_3)_2.2CuO.20H_2O$, from mono-K urate and $CuSO_4$ when either is present in excess; its properties are similar to those of the Ni salts, it is also insol. in NH_4OH and changed from greenish brown to white by the action of NaOH. It is noteworthy that the compd. formed with $CuSO_4$ is different in compn. from that formed when $(AcO)_2Cu$ is used. A. P. LOTHROP

Action of bromine on the allyl phosphates in aqueous solution: transformation of monoallylphosphoric acid to the diester, α,γ-monoglyceryl phosphate. OCTAVE BAILLY. *Bull. soc. chim.* **29**, 280–3(1921).—When treated dropwise in H_2O with Br, $PO(ONa)_2(OCH_2CH:CH_2)$ fixes 1 mol. of Br to form the *dibromohydrin* of the corresponding glycerylphosphoric acid, $PO(ONa)_2(OCH_2CHBrCH_2Br)$. This then hydrolyzes as fast as it is formed into HBr and the *monobromohydrin*, $PO(ONa)_2[(OCH_2CH(OH)-CH_2Br]$. If Na_2CO_3 is now added exactly to neutralize the HBr and the soln. evapd. or heated in an autoclave at 120°, the 2nd Br atom is also split off without any appreciable hydrolysis of the ester grouping. This last step of the reaction takes place also on merely warming the soln. and can be accurately followed by analyzing a part of the soln. from time to time for NaBr and titrating for the H_3PO_4 detectable with phenolphthalein. It is found that there is a gradual increase of NaBr with a parallel decrease of the acidity, the agreement between the two being closer the lower is the temp. to which the soln. is subjected. The last is believed to be an intramol. reaction: $O:P(ONa)_2OCH_2CH(OH)CH_2Br \rightarrow O:P(ONa).O.CH_2.CH(OH).CH_2.O$ yielding, the *diester, α,γ-monoglyceryl phosphate.* A. T. FRASCATI

Ring closure in polycarboxylic acids. II. Course of the amidation in ethanetetracarboxylic, ethanehexacarboxylic, methanetri- and methanetetracarboxylic esters. ERNST PHILIPPI, JULIE HANUSCH AND ANTON VON WACEK. Univ. Wien. *Ber.* **54B**, 895–902(1921); cf. *C. A.* **14**, 3672.—When 12 cc. dry liquid NH_3 and 10 g. $[CH(CO_2Et)_2]_2$ cooled with CO_2-Me_2CO are sealed in a tube and allowed to stand 3 days, there sep. long transparent crystals which over H_2SO_4 soon become turbid and opaque and lose NH_3, falling to a white powder. The freshly prepd. crystals yield on analysis values corresponding to those for $[CH(CONH_2)_2]_2$ and the powder resulting from its decompn. over H_2SO_4 is *2,5-diketopyrrolidine-3,4-dicarboxamide;* this, heated *in vacuo* in a slow current of dry air at200°, loses another mol. of NH_3 and gives 30% of ethanetetracarboxylic diimide (2,5-diketopyrrolidine-3,4-dicarboximide). A repetition of Mulliken's work (*Am. Chem J.* **15**, 527(1893)) confirmed his observation that $[C(CO_2Et)_3]_2$ can be prepd. only by electrosynthesis; by the following modification of his method, the yield was increased to 20%: 15 g. $NaC(CO_2Et)_3$ in 30 cc. H_2O are electrolyzed in a Pt crucible (cathode) with a Pt spiral anode and an av. current of 4 amp. at 9 v. for about 1.5 hrs., then neutralized with dil. H_2SO_4, extd. with Et_2O, freed from $CH_2(CO_2Et)_2$ and $CH(CO_2Et)_3$ *in vacuo* and crystd. fromEt_2O; attempts to amidate it either as above with liquid NH_3 or with alc. NH_3 up to 150° yielded only the unchanged ester. $CH(CO_2Et)_3$ was prepd. by the method of Scholl and Egerer (*C. A.* **7**, 2208) but by pro-

longing the heating the yield was increased to 80%. When allowed to stand 3 days with liquid NH_3 it yielded $CH_2(CONH_2)_2$ and H_2NCO_2Et almost quant. $C(CO_2Et)_4$ (8 g. from 20 g. $NaC(CO_2Et)_3$ by S. and E.'s method) behaved similarly on amidation. C. A. R.

Rotation phenomena of dextrose in solutions of tertiary sodium phosphate. Mutarotation as an analytical method. HANS MURSCHHAUSER. *Biochem. Z.* **117**, 215–26 (1921); cf. *C. A.* **15**, 524.—M. reports the influence of Na_3PO_4 on the velocity of mutarotation of aq. dextrose solns. Solns. of $M/3$ $Na_3PO_4.12H_2O$ were used. Five % dextrose solns. were made up in cond. H_2O or in solns. of phosphate in cond. H_2O and the polarization was read every 5 mins. The temp. was strictly regulated to 20.4°. The concn. of the Na_3PO_4 solns. ranged from 0.1 N to 0.000125 N. Tables and a chart are given of the results. The following table is a summary:

	H_2O	$\frac{N}{8000}$.	$\frac{N}{5000}$.	$\frac{N}{4000}$.	$\frac{N}{3000}$.	$\frac{N}{2000}$.	$\frac{N}{1500}$.	$\frac{N}{1000}$.	$\frac{N}{700}$.	$\frac{N}{500}$.
Velocity const.	6.66	7.62	10.23	11.10	14.68	23.25	30.85	45.3	60.5	99.5
Reaction time in minutes	260	210	165	155	110	75	55	37.5	28	17

When plotted these results show practically a line relationship. When the values are compared with those previously obtained for Na_2HPO_4 and NaH_2PO_4 the conclusion is justified that the effect is due to the OH ion. The differences in the consts. for the 3 salts affords a means for their analytical differentiation and detn. of purity. F. S. H.

***d*-Ribohexosaminic acids.** P. A. LEVENE AND E. P. CLARK. Rockefeller Inst. *J. Biol. Chem.* **46**, 19–33(1921); cf. *C. A.* **13**, 1214.—The two epimeric hexosaminic acids derived from ribose have been synthesized, thus completing the series of *d*-hexosaminic acids. As was the case with the other acids of the series, the predominating acid is the *l*-acid, the same as on the addition of HCN to ribose and on deamination a change of sign occurs when HNO_2 acts on the acid but not when it acts on the lactone. If the assumption is made that the hexosaminic and hexonic acids of the same sign have the α-C atom of an analogous configuration, *d*-ribohexosaminic acid may be considered as α-aminoallonic and *l*-ribohexosaminic acid as α-aminoaltronic acid. There is a remarkable identity in the numerical value of the rotation of the α-C atom in the hexonic and hexosaminic acids. *l-d-Ribohexosaminic acid*, thin plates resembling cholesterol, sol. in H_2O, insol. in the usual org. solvents, m. 212° (decompn.), $[\alpha]_D^{20}-26.0°$. *Lactone hydrochloride*, m. 188°, $[\alpha]_D^{20}-11.0°$. *d-d-Ribohexosaminic acid*, m. 186°, $[\alpha]_D^{20}+12.5°$; *lactone hydrochloride* m. 150°, $[\alpha]_D^{20}+21.5°$. *Ethyl dibenzal-d-dibohexosaminate hydrochloride*, obtained from the acid in abs. alc. by the action of BzH and dry HCl, long needles, m. 221°, $[\alpha]_D^{20}$—26.0° in MeOH. On oxidation with HNO_3 the *l*-acid yields α,α-anhydroallomucic acid and the *d*-acid α,α-anhydrotalomucic acid. All m. ps. are uncor. Improved directions for the prepn. of ribose from yeast nucleic acid are given.

A. P. LOTHROP

The utilization of the molecular refractive coefficient for the determination of the constitution of organic compounds. FRITZ EISENLOHR. *Z. angew. Chem.* **34**, Aufsatzteil, 266–8(1921); cf. *C. A.* **15**, 2079.—E. gives examples of how the value for E and the refractive index may be calcd. for a complex compd. from a simpler one. The E value of hydrocarbons + (−0.35) gives approx. the E value for the corresponding alc. or ketone. Values are also given for cyclohexenes from cyclohexanes. C. J. WEST

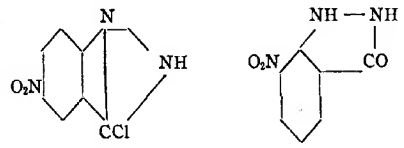
Halogen derivatives of ethylmethylbenzene. ALPHONSE MAILHE. *Bull. soc. chim.* **29**, 290–4(1921).—Ethylmethylbenzene (A), b. 159–60°, was prepd. by catalysis of oil of turpentine over finely divided Cu at 600°. To show that the compd. was the *m*-deriv., a 20-g. sample was oxidized by refluxing 6 hrs. with dil. HNO_3 (1:2). Cooling of the soln. brought down white crystals of m-$C_6H_4(CO_2H)_2$ which m. >300° and then

sublime. Its structure was further proved by nitrating A with mixed acid. From the viscous product thus obtained, Et_2O pptd. a white powder, m. 215°, recognized as the *1,3-dinitrobenzenedicarboxylic acid*. A was chlorinated by passing Cl into 100 g. of the hydrocarbon and 10 g. I for 45 min. with cooling; the chlorinated product was treated with dil. soda, washed with H_2O, dried over fused $CaCl_2$ and rectified. Unchanged A was recovered, then a fraction b. 190–200°. Above this temp. the liquid began slowly to decomp. Fractionation of the 190–200° fraction yielded *chloromethylethylbenzene* (B), b. 200–2°. To det. the position of the Cl, B was oxidized by heating for 6 hrs. on the sand bath with dil. HNO_3. White crystals were obtained, which, washed with H_2O, dried and recrystd. from boiling alc., formed brilliant needles, m. 207–8°, corresponding to the *6-chloro-m-toluic acid*, showing the Cl to have entered the 6-position. The fraction b. >220° with slow decompn. under atm. pressure was rectified *in vacuo*. This proved to be *dichloroethylmethylbenzene*, b_{60} 180°, white needles from boiling alc., m. 126°. By analogy, the 2nd Cl atom should have entered the 4-position. By adding a fresh quantity of I to the fraction b. >250° and chlorinating further, *trichloroethylmethylbenzene* (C) was obtained, silky needles, m. 205°, from boiling alc. By analogy, C should have been the 2,4,6-deriv. By passing Cl until fumes of HCl were no longer evolved into a suspension of C in CCl_4 containing 15 g. I, and subsequently washing the soln. with Na_2CO_3 and H_2O and evapg. the solvent, *tetrachloroethylmethylbenzene* was obtained, needles from alc., m. 158°. *Bromoethylmethylbenzene* (D) can be prepd. by the action of Br on cold A in the presence of flowers of S. It is very easily made by treating A dropwise with the theoretical amt. of Br in the presence of a few crystals of I, washing the resulting liquid as usual and fractionating *in vacuo*. The 1st fraction, b_{60} 135–50°, upon further rectification yields D, b. 220–1. When D is oxidized similarly to B, it gives *6-bromo-m-toluic acid*, white powder, m. 203°; recrystd. from boiling alc., m. 209°. The action of Br in excess upon A produces *dibromoethylmethylbenzene*, needles from boiling alc., m. 210°, which, from analogy, was assumed to be the 4,6-deriv. A. T. Frascati

Influence of nitro groups on the reactivity of substituents in the benzene nucleus. III. The partial reduction of the dinitrotoluenes by stannous chloride and hydrochloric acid. Harold Burton and James Kenner. Univ. Sheffield. *J. Chem. Soc.* **119**, 1047–53(1921); cf. *C. A.* **14**, 2916.—The replacement of the NO_2 group by NH_2 in di-NO_2 compds. is dependent upon the reagent employed. Thus, 3,4-$(O_2N)_2C_6H_3Me_2(o)$, with NH_3 and alc. gave 3-nitro-*o*-4-xylidine; with $SnCl_2$, on the other hand, 4-nitro-*o*-3-xylidine. Similarly, 2,3-$(O_2N)_2C_6H_3Me$, which with alc. NH_3 gives 3-$NO_2C_6H_3(NH_2)Me$, gives *2-nitro-m-toluidine*, deep red prisms, m. 107–8°, when reduced with $SnCl_2$. *2-Nitroaceto-m-toluidide*, transparent prisms, m. 126°. The constitution follows from the action of NH_3 upon the corresponding 2,3-$(O_2N)ClC_6H_3Me$ at 200° for 8 hrs. In the case of 3,4-$(O_2N)_2C_6H_3Me$, the same mixt. of isomers is obtained by treatment with alc. NH_3 or with $SnCl_2$. In the case of the 2,5-$(O_2N)_2$ deriv. the product of the action of NH_3 contained 88% 5-NO_2 deriv., while that from the action of $SnCl_2$ contained 68%, the other isomer being the 6-NO_2 deriv. This behavior is explained by the supposition that the reduction of the NO_2 compd. is preceded by the formation of an additive compd. of the NO_2 compd. with a mol. of H or of the reducing agent. It would then be expected that, of two NO_2 groups, that one would suffer preferential reduction which is the more liable to form the necessary addition product. From the previous work, however, it would appear that, of two NO_2 groups, that which suffers replacement under the influence of alc. NH_3 or of MeONa will be the more resistant to reduction. **IV. The condensation of ethyl 3- and 5-nitro-2-chlorobenzoates with hydrazines.** James Kenner and Ernest Witham. *Ibid* 1053–8.—$N_2H_4.H_2O$ and 2,5-$Cl(O_2N)C_6H_3CO_2Et$ gave a mixt. of *4-nitrocarbethoxyphenylhydrazine*, $C_9H_{11}O_4N_3$, yellow needles, m. 172° (*acetate*,

$C_{11}H_{12}O_4N_2$, faintly green needles, m. 191.5°; *benzaldehyde derivative*, $C_{16}H_{12}O_4N_2$, prismatic needles, m. 165–6°), and *5-nitro-3-keto-1,3-dihydroindazole*, $C_7H_5O_3N_3$ (A) by acidification of the filtrate, small reddish brown aggregates of prisms, m. 273° (decompn.); *acetate*, $C_9H_7O_4N_3$ small, faintly yellow prisms, m. 239°; *sodium salt*, dark orange-red powder; reduced with Sn and HCl, the *hydrochloride of the 5-amine derivative* $C_7H_7ON_3.2HCl$, was obtained as needles, m. 286° (decompn.), which become slate color on keeping. The action of $PhNHNH_2$ on $2,5\text{-}Cl(O_2N)C_6H_3CO_2Et$ gave *4-nitro-2-carbethoxyhydrazobenzene* (B), $C_{15}H_{15}O_4N_3$, yellow prisms, m. 133°, which on oxidation with HgO gave *4-nitro-2-carbethoxyazobenzene*, red, hexagonal plates, m. 70–1°. Boiling B with 0.5 *N* NaOH for 20 min. gave *5-nitro-3-keto-2-phenyl-1,3-dihydroindazole*, $O_2NC_6H_3.NH.NPh.CO$ (C),

faintly green needles, m. 270–3°. *Sodium salt*, dark brownish red cryst. ppt. *3-Chloro-5-nitroindazole*, (I) was prepd. by heating A with $POCl_3$ 5 hrs. at 120–30°; it forms faintly yellow needles, m. 210–1°. *3-Chloro-5-nitro-2-phenylindazole*, $C_{13}H_8O_2N_3Cl$, as above from C, small prisms, m. 165°. *7-Nitro-3-keto-1,3-dihydroindazole* (II),



I II

by the action of $N_2H_4.H_2O$ on $2,3\text{-}Cl(O_2N)C_6H_3CO_2Et$, Cu-colored plates from glacial AcOH, m. 290°. *Acetate*, brown needles, m. 196–7°. *Sodium salt*, $PhNHNH_2$ gave *2-nitro-6-carbethoxyhydrazobenzene*, $C_{15}H_{15}O_4N_3$, greenish yellow needles, m. 119°, which are not oxidized by HgO. *7-Nitro-3-keto-2-phenyl-1,3-dihydroindazole*, $C_{13}H_9O_3N_3$, minute greenish yellow prisms, m. 185°. *Sodium salt*, gives a purple soln. and has a tendency to sublime at 140°. C. J. West

The solubility and volatility of the chloro- and nitro anilines and of their acetyl derivatives. Nevil V. Sidgwick and Howard E. Rubie. Oxford. *J. Chem. Soc.* 119, 1013–24(1921).—The $ClC_6H_4NH_2$ are a normal group of isomers. Their vapor pressures do not differ to any marked extent; their solubilities in H_2O are of the same order and the rise of the heat of soln. in C_6H_6 is small, even with the *p*-compd. The introduction of an Ac group increases the difference between the isomers but not very greatly. The $O_2NC_6H_4NH_2$ are distinctly abnormal, although not much more so than the ClC_6H_4NHAc. The differences are in the usual direction. The introduction of an Ac group again accentuates the differences and the $O_2NC_6H_4NHAc$ show marked abnormality. As regards the properties considered $PhNH_2$ and PhNHAc resemble BzOH rather than PhOH in that their Cl derivs. are normal, while the ClC_6H_4OH are not. All these compds. form abnormal NO_2 derivs.; the abnormality of the $O_2NC_6H_4NH_2$ and $O_2NC_6H_4NHAc$ is of the same type as that of the $HOC_6H_4CO_2H$ and the $O_2NC_6H_4OH$ and does not present the peculiarities which occur among the $O_2NC_6H_4CO_2H$. C. J. West

Action of chloroform on phenylhydrazine. W. Leigh Barnett. *J. Soc. Chem. Ind.* 40, 167–8T(1921).—The reaction product of $CHCl_3$ upon $PhNHNH_2$ is $(PhNHNH_2Cl)_2CH$, scales, decomp. 221°, very unstable and decompg. in the presence of H_2O into $PhNHNH_2.HCl$ and HCO_2H. C. J. West

Aminohydrazines. VI. Acetophenone *p*-aminophenylhydrazone and *p*-aminophenylhydrazine. Hartwig Franzen and Paul Steinführer. Techn. Hochschule Karlsruhe. *Ber.* **54B**, 861–7(1921); cf. *C. A.* **13**, 423.—*Acetophenone p-aminophenylhydrazone* (A) (23 g. from 40 g. of the NO_2 compd. in 800 cc. boiling alc. and 150 cc. alc.

NH_3 slowly treated, with vigorous turbining, with 145 g. $Na_2S_2O_4$ in 580 cc. H_2O until the color changes from red-brown to lemon-yellow, filtered, treated with 50 cc. NH_4OH and then to permanent turbidity with almost boiling H_2O (2.25 l.) and allowed to stand 12 hrs.), faintly yellow leaflets, m. 134–6° (decompn.), relatively easily sol. in boiling org. solvents with partial decompn., evolves the odor of PhCOMe in a few hrs., becomes brown and tarry in 3 days and changes completely into a brown tar in 2 weeks. When 6.75 g. **A** is covered with 50 cc. alc. and 25 cc. of cold satd. alc. HCl and the resulting thick magma of the HCl salt is boiled 45 min., whereupon it becomes brown, filtered and dried, it yields 5.5 g. of a clay-yellow substance, and the brown-yellow filtrate on steam distn. gives PhCOMe in abundance. The clay-yellow substance dissolves easily in H_2O and on addition of alkali and heating gives off much NH_3; on crystn. from dil. alc. it yields 3.65 g. *p*-$C_6H_4(NH_2.HCl)_2$. *Benzylideneacetophenone p-aminophenylhydrazone* (2.35 g. from 2 g. A in 50 cc. alc. and 1 g. BzH), lemon-yellow needles from alc., m. 178–80° (gas evolution); *m-nitro derivative*, from $O_2NC_6H_4CHO$, red cryst. powder from C_5H_5, m. 177–9°; *thiocarbanilide*, $PhCMe{:}NNHC_6H_4NHCSNHPh$, from 2 g. A in 30 cc. boiling alc. and 1.2 g. PhNCS, leaflets from $CHCl_3$, m. 166–7° (gas evolution). When 5 g. of finely powdered A are shaken vigorously with 500 cc. of 10% HCl and the intensely yellow soln., cooled in ice H_2O, is treated with 500 cc. concd. HCl in small portions there gradually seps. 86% of *p-aminophenylhydrazine dihydrochloride* (B), fine, faintly yellow needles, easily sol. in cold H_2O, forming intensely lemon-yellow dil. and orange-yellow concd. solns. which soon decomp. at room temp. with faint evolution of gas and reddening; in sealed vessels the solid is stable for some time but in a few weeks decomps. to a dark tar; 1.9 g. in 75 cc. H_2O vigorously shaken with 2.6 g. anisaldehyde and 150 cc. cold satd. NaOAc yields 2.5 g. *di-[p-methoxybenzylidene]-p-aminophenylhydrazone*, greenish yellow cryst. powder from C_6H_6, m. 181–2°. *Pyruvic acid p-aminophenylhydrazone* (1.5 g. from 2.94 g. B in 30 cc. H_2O, 1.5 g. $AcCO_2H$ in 10 cc. H_2O and 12 g. NaOAc in 60 cc. H_2O), grayish powder, m. 145–7° (very vigorous gas evolution), sol. in boiling H_2O and alc. with yellow color soon changing to brown, gradually decomps. on standing (m. p. after 3 weeks, 136–8°) and on attempted recrystn. from alc. gives a product m. 133–5°. *Tribenzoyl-p-aminophenylhydrazine* (2 g. from 2 g. B and 5 cc. BzCl boiled 75 hrs. in 50 cc. C_5H_5) gray cryst. powder, m. 236–7°. The decompn. of A by hot alc. HCl may be represented by the equation $H_2NC_6H_4NHN{:}CMePh+H_2O+H_2=C_6H_4(NH_2)_2+PhCOMe+NH_3$. As no indole was obtained by the HCl decompn. A was boiled in xylene and cumene but most of it was recovered unchanged. It was then heated a long time at 200° in a H atm.; 0.5 mol. NH_3 and 0.66 mol. N_2 per mol. A are given off but no cryst. substance could be isolated from the residue. If any indole is formed under the above conditions, it is not the only reaction but is accompanied by other decompn. phenomena. C. A. R.

Preparation of 5,5′-mercuribis-3-nitro-4-hydroxyphenylarsonic acid. JULIUS STIEGLITZ, MORRIS KHARASCH AND MARTIN HANKE. *J. Am. Chem. Soc.* **43**, 1185–93 (1921).—As the effectiveness of salvarsan and neosalvarsan against spirochetes has been found to be greater when their administration is alternated with that of mercurials, the authors undertook to prep. a compd. which should contain both As and Hg, each combined with C, in the same mol. In the course of the work, interesting theoretical questions developed (such as the replacement of an AsO_3H_2 group in aromatic compds. by H by means of $Na_2S_2O_4$ and the instability of certain substituted $HgPh_2$ derivs. in alk. soln.) which will be discussed in a later paper by K. 3,4′,5-$O_2N(HO)(AcOHg)$-$C_6H_2AsO_3H_2$ (A) was prepd. by the method of Raiziss, Kolmer and Gavron (*C. A.* **15**, 408) except that 1 cc. glacial AcOH was used for each 10 g. of the original $O_2N(HO)C_6H_3$-AsO_3H_2 and the reaction was allowed to proceed 3.5 instead of 1.5 hrs. The position of the AcOHg group was detd. by slowly treating 5 g. of A in 120 cc. H_2O with 2.6 g.

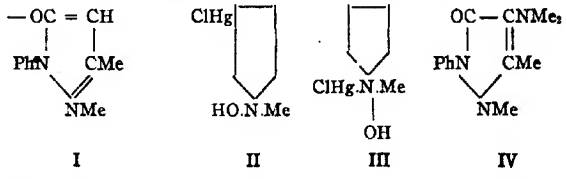
I and 4 g. KI in 30 cc. H_2O and heating 1 g. of the resulting *3-nitro-4-hydroxy-5-iodophenylarsonic acid* (very hygroscopic light yellow powder, easily sol. in dil. NaOH and Na_2CO_3 with deep red color) in 0.66 cc. of 15% NaOH and 3 cc. H_2O 4 hrs. on the H_2O bath under a reflux with 2 g. KI in 2 cc. dil. H_2SO_4; the product was $4,6,2\text{-}I_2(O_2N)C_6H_2OH$, m. 97°. A (12 g.) in 150 cc. H_2O boiled 15 min. with 18 g. $Na_2S_2O_3$ gave 0.6 g. *6,6'-mercuribis-2-nitrophenol*, light yellow ppt. sol. in NaOH with red color, does not m. 295°; when the Hg is replaced by I in the usual way, the compd. yields $6,2\text{-}I(O_2N)C_6H_3OH$, m. 110°. The main product in the above reaction is decompd. by NaOH into HgS, Na_2SO_4 and a $HgPh_2$ deriv., whence the authors infer that a Hg thiosulfate complex is formed. There were also indications of some loss of As and that some S attached itself to the ring as the result of the treatment with $Na_2S_2O_3$. Next, 4 g. A in 30 cc. H_2O and 6 cc. of 15% NaOH were heated 0.5 hr. on the H_2O bath with 2 cc. *N* NaSH, again treated with 2 cc. NaSH and heated 0.5 hr. longer and the addition of NaSH (in 0.5-cc. portions at 15-min. intervals) and heating repeated until the soln. gave a negative stannite test (see below), when the soln., filtered hot, was treated with $(NH_4)_2SO_4$, yielding the *ammonium salt*, golden yellow flakes, of *5,5'-mercuribis-3-nitro-4-hydroxyphenylarsonic acid*, very hygroscopic yellow powder; yield, 78%. In testing for the completeness of the "bridging" of the 2 halves of the mol. through the Hg, it was found that as little as 0.1 mg. of the unbridged compd. A in 1 cc. can be detected by the cloud of pptd. Hg which it forms when treated with Na_2SnO_2, while the bridged compd., similarly treated, remains perfectly clear at any concn. CHAS. A. ROUILLER

Derivatives of sulfur in commercial salvarsan. I. HAROLD KING. National Inst. Med. Research. *J. Chem. Soc.* **119**, 1107–20(1921).—Farger and Pyman (*C. A.* **14**, 2481) isolated 3,3'-diamino-4,4'-dihydroxyarsenobenzene from com. salvarsan and showed that the S enters the mol. during the 1st stage of reduction. 106 g. $3,4\text{-}O_2N(HO)C_6H_3AsO_3H_2$ in 800 cc. *N* NaOH at −2° was treated with 216 g. $Na_2S_2O_4$ in 4 portions, the temp. being reduced to −2° before each addition. On standing overnight $3,4\text{-}H_2N(HO)C_6H_3AsO_3H_2$ sepd. (48 g.). The filtrate, acidified with HCl (120 cc.), deposited a ppt. after standing about 1 week; this was washed with H_2O at 40° to remove Na_2SO_4, dissolved in NH_4OH and treated with 4% $CaCl_2$. *3,3-Diamino-4,4'-dihydroxy-5,5'-disulfinoarsbenoenzene* (A), $C_{12}H_{12}O_6N_2As_2S_2$, ppts. as the Ca salt; acidified with HCl, it forms a dark brown brittle mass, fawn-colored after drying, insol. in acids but sol. in alkalies. The yield was 2.75 g. The filtrate contains *3-amino-4-hydroxy-5-sulfinophenylarsonic acid* (B), $C_6H_8O_6NaAs$, minute elongated plates with pointed ends, which appear unchanged at 280°; insol. in acids, it dissolves with a bright yellow color in $NaNO_2$ and then couples with alk. $\beta\text{-}C_{10}H_7OH$ with the production of a deep reddish brown sol. dye. The NH_4OH soln. does not give a ppt. with LiCl, $CaCl_2$, or magnesia mixt. but gives a heavy ppt. of spherocrystals with $BaCl_2$. 10 g. B, treated with 36 cc. 3 % H_2O_2, gave a quant. yield of *3-amino-4-hydroxy-5-sulfophenylarsonic acid* (C), $C_6H_8O_7NSAs$, decomp. 258°, sol. in 4 parts boiling H_2O; HNO_2 produces a deep yellow soln., which couples with $\beta\text{-}C_{16}H_7OH$ with the production of a deep reddish brown sol. dye. It reduces Ag_2O. The NH_4OH soln. gives a cryst. salt with $CaCl_2$ and a white ppt. with magnesia mixt. $BaCl_2$ ppts. an oil which dissolves on heating and a *barium salt* seps. as rosets of crystals. $Ba(OH)_2$ does not give a ppt. of $BaSO_4$ but a cryst. Ba salt. Upon reduction of B with $Na_2S_2O_4$, A is formed, but a more pure product may be obtained by using H_3PO_2 at 100° (a trace of KI aids). A good yield of $o\text{-}O_2NC_6H_4OH$ is obtained by boiling $3,4\text{-}O_2N(HO)C_6H_3AsO_3H_2$ with concd. $NaHSO_3$. The reduction of an equimol. mixt. of B and $3,4\text{-}H_2N(HO)C_6H_3AsO_3H_2$ with $Na_2S_2O_4$ gave *3,3'-diamino-4,4'-dihydroxy-5-sulfinoarsenobenzene hydrochloride*, $C_{12}H_{13}O_4N_2SAs_2.HCl$ (D), though better yields were obtained with H_3PO_2. The reduction of C with H_3PO_2 gave *3,3'-diamino-4,4'-dihydroxy-5,5'-disulfoarsenobenzene*,

$C_{12}H_{12}O_8N_2S_2As_2$, insol. in H_2O, does not form salts, sol. in alkali but pptd. by an excess, owing apparently to a coagulating action of the HO ion. The NH_4OH soln. gives a ppt. with $CaCl_2$, $BaCl_2$, magnesia mixt. and with $La(NO_3)_3$ and $Th(NO_3)_4$. Upon hydrolysis, *6-aminophenol-o-sulfonic acid* results, $C_6H_7O_4NS$, long silky needles with 0.5 H_2O, which forms a difficultly sol. Ba salt, and does not form a sparingly sol. diazo-oxide. *3,3'-Diamino-4,4'-dihydroxy-5-sulfoarsenobenzene hydrochloride*, by the reduction of a mixt. of 1.15 g. B and 0.85 g. 3,4-$H_2N(HO)C_6H_3AsO_3H_2$ in a mixt. of 10 cc. H_3PO_2, 5 cc. H_2O and 5 cc. glacial AcOH at 60°; slowly sol. in H_2O, sol. in 2 *N* NaOH but pptd. by an excess; sol. in dil. or concd. NH_4OH. *3,3'-Diamino-4,4'-dihydroxy-5-sulfinoarsenobenzene*, $C_{12}H_{12}O_7N_2As_2S_2$. The MeOH-insol. part of comm. salvarsan is a mixt. of **D** and "salvarsan sulfate" and "hydrochloride." There is no evidence of the presence of a monosulfamic acid as suggested by F. and P. C. J. WEST

Action of sublimate upon salvarsan and neosalvarsan. A. BINZ AND H. BAUER Frankfurt a. M. *Z. angew. Chem.* **34**, Aufsatzteil, 261–3(1921).—22 g. $HgCl_2$ in 220 cc. H_2O and 10 g. salvarsan in 100 cc. H_2O gave 7.7 g. $HO(NH_2)C_6H_3AsO$, isolated as the HCl salt. When an excess of salvarsan is used, metallic Hg is formed. In general it is true that upon mixing salvarsan with slightly alk. solns. of $HgCl_2$, there is produced an equiv. amt. (to the $HgCl_2$) of aminophenylarsenious oxide. 5 g. neosalvarsan, treated with varying amts. of $HgCl_2$ gave the following products: with 0.25 g. $HgCl_2$, 2.8 g. neosalvarsan acid, 0.2 g. dihydroxyamino(iminomethylene sulfurous acid)-arsenobenzene (**A**); the latter is obtained by reduction of the oxide. With 1.87 g. $HgCl_2$ 1.94 g. **A** are obtained direct and 0.45 g. from the oxide. With 3.75 g. $HgCl_2$, 1.06 g. **A** are obtained directly and 2.9 g. from the oxide; while with 7.5 g. $HgCl_2$ only 1.1 g. **A** were obtained from the oxide. **A** may be prepd. by adding 6 g. $HgCl_2$ in 50 cc. H_2O to 6 g. neosalvarsan in 50 cc. H_2O, removing the Hg, treating with HCl, adding 3 g. Na_3PO_2, and allowing to stand 12 hrs. C. J. WEST

Some compounds of antipyrine with mercury. E. OLIVERI-MANDALÀ. Univ. Palermo. *Gazz. chim. ital.* **51**, I, 125–30(1921).—Antipyrine (**A**) gives 2 types of compds. with Hg halides: $C_{11}H_{12}N_2O.HgR_2$ and $(C_{11}H_{12}N_2O)_2HgR_2$. The 1st is obtained by mixing the reagents in equimol. amts. The 2nd is obtained by working in the presence of the halogen acid. The expts. here described show that **A** also adds unstable groups like HgClOH, HgIOH, $HgClNH_2$. Astre and Ville (*Bull. soc. chim.* [3] **33**, 842(1905)) found that 1 mol. $Hg(OH)_2$ adds 2 of **A** in aq. suspension. On the basis of these observations O.-M. prefers the unsatd. formula I of Knorr and Michaelis for **A** and believes that the negative part of the mol. added is attached to N



I II III IV

while the rest is bound to the O as is represented in II rather than as in III, which is the usual formula given for this type of product. Tests with pyramidone (IV) showed that although it adds some $HgCl_2$ it does not add $Hg(OH)_2$, HgClOH nor $HgClNH_2$ under the conditions used with **A**. This O.-M. considers, supports the interpretation given above and is due to the fact that the NMe_2 group in IV destroys the mobility of the methinic H in the group OC:CH:CMe:NMe of **A**. To 5.6 g. **A** in 100 cc. H_2O an excess of NH_4OH was added and then 14 g. $HgCl_2$ gradually. The mixt. was heated several hrs. on the H_2O bath and filtered from pptd. Hg. The filtrate on evapg. *in vacuo*

over H_2SO_4 gave an oil which crystd. from EtOH, giving $C_{11}H_{12}N_2O.HgClNH_2$. This compd. with H_2S ppts. HgS, gives no HgO with alkalies and alkali carbonates, gives no reaction with NH_4OH; dil. HCl gives a white ppt. that dissolves in excess. $FeCl_3$ gives a red color and $NaNO_2$ in the presence of AcOH gives a blue-green color. The last 2 reactions are characteristic of A. 9.4 g. A in 150 cc. H_2O were heated with 13.5 g. $HgCl_2$ and 40 cc. *N* NaOH for 1 hr. on the H_2O bath. The soln. was filtered and on cooling sepd. small crystals of $C_{11}H_{12}N_2O.HgClOH$, m. 93°, identical with that obtained by Paderi (*C. A.* **14**, 774). Sublimed HgI_2 reacts under the same conditions to give $C_{11}H_{12}N_2O.HgIOH$, as yellowish scales, m. 135°. E. J. WITZEMANN

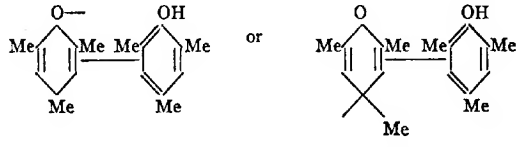
3-nitro-4-hydroxy-5-iodobenzoic acid and the mercury derivative of *p*-hydroxy-*m*-nitrophenylcarbinol. MORRIS S. KHARASCH. *J. Am. Chem. Soc.* **43**, 1203–5(1921).—Hart and Hirschfelder obtained from $4,3\text{-HO}(O_2N)C_6H_3CH_2OH$ a Hg deriv. to which, from the fact that it forms no anhydride at 110°, they assigned the structure $4,3,6\text{-HO}(O_2N)(HOHg)C_6H_2CH_2OH$, *i. e.*, with the Hg in the *m*-position to the HO group (*C. A.* **15**, 679). This is in such marked disagreement with the position assumed by the Hg in the mercuration of nitrophenols that K. undertook to obtain direct evidence as to the structure of their compd.; 3.4 g. of the compd. in 75 cc. H_2O was treated with 21 cc. KI_3 (0.1 g. I per cc.) and shaken until the color of the I disappeared (1.5 hrs.). This gave 1.8 g. *3-nitro-4-hydroxy-5-iodophenylcarbinol*, yellow needles from very dil. alc., m. 138°, oxidized by excess of alk. $KMnO_4$ to $5,4,3\text{-I(HO)}(O_2N)C_6H_2CO_2H$ (Weselsky, *Ann.* **174**, 110(1874)), m. 251°, identical with the product obtained by treating $5,4\text{-I(HO)}C_6H_3CO_2H$ in a large vol. of hot H_2O with dil. HNO_3 and boiling 15 min. In H. and H.'s compd., therefore, the Hg is in position 5 or in the *o*-position to the HO group. CHAS. A. ROUILLER

The physical chemical study of the so-called hydroxyazo compounds. E. PUXEDDU AND M. GENNARI. Univ. Cagliari. *Gazz. chim. ital.* **51**, I, 147–52(1921).—In spite of much work the constitution of the so-called hydroxyazo compds. is still open to discussion. Besides the tautomeric azophenolic and quinonehydrazonic formulas for these compds. their physical chem. behavior has caused them to be considered as pseudo acids indifferent to indicators, non-electrolytes that are incapable of giving NH_4 salts in the absence of ionizing solvents. Thus Goldschmidt and Brubacher (*Ber.* **24**, 2300(1891)) found that on reduction of the Ac derivs. of many *o*-hydroxyazo compds. PhNHAc and $NH_2C_6H_4OH$ were obtained, which supports the quinonic formula. But these facts lost their value when it was found that acyl groups in these compds. are transported from OAc in the *o*-position to the NH group. The conclusions of Farmer and Hantzsch (*Ber.* **37**, 2089(1899)) that these compds. are quinonic in the free state and behave as pseudo acids was objected to because the cond. detns. on measured concns. of these salts could not be repeated because there was always an undissolved residue of the compd. Meanwhile P. and Oddo (*Gazz. chim. ital.* **36** (1906)) proposed the mesohydric formula, which differs from both of the above. P. and G. have resumed the physical chem. study of this problem by carrying out some observations on the mol. cond. and on the affinity consts. of these compds. The mol. cond. was detd. on the Na and K salts of various hydroxyazo compds. by the telephone method properly checked by detns. on KCl. The NaOH and KOH were especially prepd. (Küster, *Z. physik. Chem.* **13**, 134(1897)) and the cond. of the Na and K salts, obtained by dissolving the hydroxyazo compds. in the equiv. amt. of the alkali, was detd. The salts of *p*-hydroxyazobenzene, benzeneazo-*o*-cresol, benzeneazo-*m*-cresol, benzeneazo-*p*-cresol, *o*-, *m*- and *p*-tolueneazophenol were studied in this way and useful results were obtained only with *o*-tolueneazophenol (A). With the others, solns. of the Na and K salts could not be prepd. in the proportions used. These salts all undergo hydrolysis, which becomes apparent by the insoly. of the free compd. in H_2O, but the data on the degree of hydrol-

ysis are still incomplete. The value $\Delta_{1024-32} = 14.12$ was obtained with the Na salt of A, with the K salt the value is about 20. On the basis of Ostwald's expts. (*Z. physik. Chem.* **2**, 240) on the cond. of isomers these results should, it appears, be the the same. Other expts. on this subject are under way. E. J. WITZEMANN

Action of the Grignard reagent on certain organo-sulfur compounds. HARRY HEPWORTH AND HENRY W. CLAPHAM. Ardeer Factory, Stevenston, N. B. *J. Chem. Soc.* **119**, 1188–98(1921).—The action of RMgX on $PhSO_2Cl$ and $EtSO_2Cl$ lead to the formation of sulfoxides, while sulfides and in some cases sulfones were formed to a smaller extent. This method of prepn. of sulfoxides is recommended. PhMgBr and $PhSO_2Cl$ gave a small amt. of Ph_2 and Ph_2SO. The action of EtMgBr gave equal amts. of PhSOEt, PhEtS and a small quantity of $PhEtSO_2$. 20 g. $PhSO_2Cl$ with $PhCH_2MgCl$ gave 10 g. $PhSOCH_2Ph$, besides small amts. of $PhSO_2CH_2Ph$ and $PhSCH_2Ph$. 20 g. $EtSO_2Cl$, reacting with PhMgBr, gave 14 g. Ph_2SO, besides PhBr and Ph_2; EtMgBr gave Et_2SO but a larger amt. of Et_2S. The action of MeMgI upon EtSH gave *ethylthiol iodide*; C_2H_5ISMg, voluminous ppt. With BzCl this gave PhCOSEt, while $ClCO_2Et$ gave $EtSCO_2Et$, and AcCl gives MeCOSEt. PhCOSEt and MeMgBr gave $PhEt_2COH$ and EtSH. PhMgBr gave Ph_3COH. $EtSCO_2Et$ and PhMgBr gave Ph_2MeCOH. MeCOSEt and PhMgBr also gave Ph_3COH. Very little reaction occurs when MeMgI and Ph_2SO are heated in C_7H_8, some Ph_2S and unchanged Ph_2SO being obtained. The reaction of PhMgBr with Ph_2SO or iso-Am_2SO is much slower. $PhSOCH_2Ph$ and MeMgBr gave some $PhSCH_2Ph$. The sulfoxides appear to have no tendency to react in the enolic form. The sulfones do not react with RMgX. $PhSO_2CH_2CO_2Et$ reacts with the evolution of 1 mol. CH_4. C. J. WEST

Univalent oxygen. Preparation and oxidation of mesitol. C. W. PORTER AND F. H. THURBER. *J. Am. Chem. Soc.* **43**, 1194–8(1921).—Mesidine was prepd. from equimol. amts. of 1,2,4-xylidine and MeI allowed to stand 2–3 hrs. in rice, then heated in sealed tubes to 260° in the course of 1 hr. and kept at this temp. 3 hrs. On diazotization it yielded mesitol, feathery crystals from 20% alc., m. 69°, 5 g. of which, shaken 4 hrs. at 50° with 25 g. moist Ag_2O and 500 cc. C_6H_6, gave a *compound* (A) sepg. in fine red needles, forming a deep red soln. in more than 1000 parts C_6H_6, rapidly reduced to colorless products by alc. NaOH or KOH, fairly stable in very dil. acid soln. in alc., rapidly decolorized in alc. by $SnCl_2$, $TiCl_3$ and $FeSO_4$, sol. in concd. H_2SO_4 with a very deep red color discharged by diln. with H_2O, at once converted into colorless products by HNO_2, mol. wt. in freezing C_6H_6 230–71. Its compn. and the amt. of reducing agents required to decolorize the compd. indicate that it is a quinhydrone,



Regardless of the nature of the tie between the two nuclei, it is evident that the compd. contains an odd or unpaired electron—the outstanding characteristic of a free radical—for it is reduced by the addition of only one H atom per mol. C. A. R.

Influence of position on the solubility and volatility of the mono- and dinitrophenols. NEVIL V. SIDGWICK AND WILFRID M. ALDOUS. Oxford. *J. Chem. Soc.* **119**, 1001–13 (1921).—In this paper the soly. of 5 of the six $(O_2N)_2C_6H_3OH$ in H_2O and C_6H_6 are described and also their volatility in steam, together with that of $O_2NC_6H_4OH$ and picric acid. The influence of the *o*-NO_2 group in diminishing the soly. prevails and to nearly the same extent, whether the 2nd NO_2 group is in position 4, 5, or 6; whereas

if there is no *o*-NO_2 group, the soly. is much greater. The 1,2,3-compd. is near alsy sol. in H_2O as the *m,p*-isomer, which anomaly is repeated in the volatility and in the heat of soln. in C_6H_6. *o*-$O_2NC_6H_4OH$ and all the $(O_2N)_2C_6H_3OH$ (except the 1,2,3-deriv.) have a high vapor pressure, a small soly. in H_2O, and a large soly. in C_6H_6 if at least one *o*-position is occupied, and the occupation of a 2nd *o*-group does not greatly increase them, while those compds. in which neither *o*-position is occupied have low vapor pressures, are much more sol. in H_2O and show a much larger increase of the heat of soln. in C_6H_6.

C. J. WEST

Influence of position on the solubilities of the substituted benzoic acids. NEVIL V. SIDGWICK AND ELINOR K. EWBANK. Oxford. *J. Chem. Soc.* 119, 979–1001(1921); cf. *C. A.* **14**, 2482.—The soly. of *o*-, *m*- and *p*-$HOC_6H_4CO_2H$, $(HO)MeC_6H_3CO_2H$, $O_2NC_6H_4CO_2H$ and $ClC_6H_4CO_2H$ in H_2O and C_6H_6 and in some cases EtOH, BuOH and C_7H_{16} has been detd. and the results are given in tables and curves. The critical soln. temps., the nominal heats of soln. and the vapor pressure of the liquid acids also are recorded. Among the HO acids, which are typical abnormal compds., the soly. relations are reversed as we pass from H_2O to C_6H_6; the isomeride with the lowest critical soln. temp. (greatest soly.) in H_2O shows the largest increase in heat of soln. in C_6H_6. Heptane shows the same properties as C_6H_6 but in a more marked degree. The isomers with the greatest soly. in H_2O invariably have the smallest vapor pressure. The alcs. occupy a peculiar position, the soly. being abnormally high in every case. A comparison of the soly. of the three $HOC_6H_4CO_2H$ in various solvents at moderate temp. shows that the ratio *o*: *p*, which is very small in H_2O, rises as the dielec. const. of the solvent falls, reaching a max. in C_6H_6, which is yet far short of the ratio of the vapor pressures. The ratio *m*: *p*, which is very much nearer unity, tends to rise in the same direction. The *o*-acids behave like non-polar compds. and are more sol. in non-associated solvents of low dielec. power, while the *p*- and in a rather smaller degree the *m*-acids, have the opposite character. The $(HO)MeC_6H_3CO_2H$ closely resemble the $HOC_6H_4CO_2H$. The Cl derivs. are practically normal. The NO_2 acids are abnormal but in a different sense from the $HOC_6H_4CO_2H$. The differences in volatility are distinct but not large. But the solubilities, which are very different, are the reverse of what we should expect, the *o*-acid having the lowest and the *p*-acid the highest critical soln. temp. in H_2O. In C_6H_6 the soly. of the *o*- and *m*-acids are in the opposite order to those in H_2O, but the *p*-acid, although the least sol. in H_2O, is also about as insol. in C_6H_6 as the *o*-acid. Other relations are discussed and all results expressed in tables and curves.

C. J. WEST

Metallic derivatives of nitrophenolic compounds. I. Interaction of barium, strontium and calcium hydroxides with the mononitrophenols. ARCHIBALD EDWIN GODDARD. Univ. Birmingham. *J. Chem. Soc.* **119**, 1161–5(1921).—This study is made to ascertain what influence various metals have on the color of nitrophenoxides and to throw further light on the coördination numbers of the metals concerned. It may also be possible to ascribe definite formulas to metallic hydroxides of doubtful compn. on the assumption that each HO of the latter will react with one phenolic group. All the *o*-salts are red, the *m*-salts tend towards orange and the *p*-salts yellow, addition of H_2O being coincident with decrease of color. It is noticeable that no *o*-deriv. has more than 4 mols. H_2O, *m*-salts with more than 5 mols. seem unstable, while in the *p*-series, the max. is 8, and the compds. are quite stable in air. *Barium o-nitrophenoxide*, $C_{12}H_8O_6N_2Ba$, from 2 g. $Ba(OH)_2$. 8 H_2O and 1.8 g. *o*-$O_2NC_6H_4OH$ in 30 cc. H_2O, brilliant scarlet plates, do not m. 300°, sol. in warm EtOH, Me_2CO and C_5H_5N. *m-Derivative*, $C_{12}H_8O_6N_2Na.4H_2O$, orange-yellow needles. A 2nd prepn. consisted of orange needles with 5 H_2O. On heating to 170–80° for a short time, the anhydrous salt is obtained as a dull red powder, moderately sol. in AcOEt, slightly so in Et_2O. *p-Derivative*, yellow

plates when anhydrous, or yellow rhombic crystals with 8 H_2O. *Strontium o-nitrophenoxide*, from 2.7 g. $Sr(OH)_2$ and 2.8 g. o-$O_2NC_6H_4OH$ in 50 cc. H_2O, pale orange plates with 3 H_2O, which give a yellow soln. in AcOEt, and a red color in boiling $CHCl_3$. The anhydrous compd., by heating the salt at 180° for 3 hrs., is deep orange. *m-Derivative*, long vermillion needles with 4 H_2O or golden orange needles with 8 H_2O, which lose H_2O on exposure to air or in contact with org. solvents., changing to brilliant red. *p-Derivative*, small, brilliant yellow needles with 8 H_2O. *Calcium o-nitrophenoxide*, $C_{12}H_8O_6N_2Ca.2H_2O$, from 2 g. o-$O_2NC_6H_4OH$ and 0.53 g. $Ca(OH)_2$ in 50 cc. H_2O, pale orange, blunt needles or, if 4 H_2O are present, pale orange plates from which the deep red anhydrous salt is obtained by heating at 180° for 2 hrs. *m-Derivative*, reddish orange microneedles with 1 H_2O, or small rosettes of deep orange needles if anhydrous. *p-Derivative*, deep yellow when anhydrous (heating the hydrates at 220° for 1 hr.), long lemon-yellow needles with 5 H_2O, or yellow microneedles with 2.5 H_2O, glistening yellow needles with 8 H_2O, the last of which m. in its H_2O of crystn. 80–90°. On exposure to air, the 2.5 H_2O increased to 3 H_2O. C. J. West

Lichen products. III. Determination of the constitution of divarin. Adolf Sonn. Univ. Königsberg i. Pr. *Ber.* **54B**, 773–4(1921); cf. *C. A.* **11**, 2673.—Divarin (A), the phenol $C_9H_{12}O_2$ obtained by the action of alkalies or HI on certain acids isolated from lichens of the species *Evernia*, was assigned the structure 3,5-$(HO)_2C_6H_3Pr$ by Hesse. Johnson and Hodge (*C. A.* **7**, 3507), who synthesized 2,4-$(HO)_2C_6H_3Pr$ (B), give the same m. p. (82–3°) for their product as that of A. As the description of their compd. was too brief to permit of detg. whether it was identical with A, S. has repeated their synthesis: 40 g. m-$C_6H_4(OH)_2$, 18 g. EtCN and 15 g. $ZnCl_2$, in 100 cc. Et_2O were satd. with dry HCl and after some hrs. the Et_2O was poured off from the sirupy deposit or it was boiled 15–30 min. with H_2O, giving 25 g. 2,4-$(HO)_2C_6H_3COEt$. On reduction by Clemmensen's method, this yields an oil which solidifies on cooling; when taken up in Et_2O, dried with Na_2SO_4 and distd. *in vacuo* there first passes over much H_2O, which had undoubtedly been held as H_2O of crystn., then B, b_{14-5} 172–4°, which solidifies on long standing or stirring with C_6H_6 and seps. from C_6H_6 or ligroin in thin slender prisms, m. (anhydrous) 107–8°, (hydrated) 71°, gives a reddish violet color with aq. and a green-yellow color with alc. $FeCl_3$; the alk. soln. gradually becomes dark green in the air. J. and H.'s product, although apparently anhydrous from the analytical results, doubtless contained some H_2O and, therefore, melted low. When a CHO group is introduced into B by Gattermann's method (*C. A.* **2**, 820) and the crude product is heated with $PhNH_2$ there is formed *5-propyl-2,4-dihydroxybenzalaniline*, stout green-yellow prisms from 20 parts C_6H_6, m. 159°, gives a black-green color with alc. $FeCl_3$, converted by boiling in alc. with HCl under a reflux into the aldehyde, m. 71–6°. C. A. R.

Action of monomolecular formaldehyde on Grignard compounds. K. Ziegler. Univ. Marburg. *Ber.* **54B**, 737–40(1921).—Z. finds that by passing the vapors of dry distd., *i. e.*, of depolymerized, trioxymethylene (A) into vigorously turbined Grignard solns., the action of the HCHO is greatly simplified and the same reaction which requires 2–3 days when A is used (cf. Grignard, *Compt. rend.* 134, 107(1902)) can be effected in 10–5 min. As far as can be judged from the preliminary expts. thus far made the yields are as good as, if not better than, those obtained by the G. method. The A was dried 1–2 days *in vacuo* over P_2O_5 and 1.5–2.0 times the calcd. amt. distd. from a Jena retort into a Woulff bottle, containing the Grignard soln., in ice H_2O; when all the A had been vaporized (15–20 min. for 20–30 g. A), the soln. was stirred about 15 min. longer. From 80 g. PhBr, 12 g. Mg, 250 cc. Et_2O and 25 g. A was obtained 38 g. $PhCH_2OH$. α-$C_{10}H_7CH_2OH$ b_{11} 162–3° is obtained in 28 g. yield from 8 g. Mg in 30 cc. Et_2O and 3 g. EtI treated, while vigorously boiling, with 64 g. α-$C_{10}H_7Br$ in 150 cc. Et_2O, warmed 15 min. after about 0.5 hr. to complete the soln. of the Mg and at once treated with the

vapors from 25 g. A; it crysts. from petr. ether-C_6H_6 in fine needles, m. 59.5–60°, 20 g. of which on oxidation by Bamberger Lodter's method (*Ber.* **21**, 259(1888)) yields 16 g. α-$C_{10}H_7CHO$ (purified through the $NaHSO_3$ compd.), b_{11} 149.4–50.4°. Of the aliphatic alcs. Z. has thus far prepd. only PrOH from EtMgBr and HCHO; the yield was not as good as in the preceding cases, owing in part to the fact that, besides the alc., considerable $CH_2(OEt)_2$ also was formed. CHAS. A. ROUILLER

Structural isomerism of the oximes. I. Criticism of the Hantzsch-Werner hypothesis and a new theory of the constitution of isomeric oximes. FREDERICK WM. ATACK. Univ. Manchester. *J. Chem. Soc.* **119**, 1175–84(1921).—The Hantzsch-Werner hypothesis of the stereoisomerism of oximes is criticized in view of the fact that it fails to explain characteristic reactions of the so-called *syn-* and *anti*-oximes, their mode of interconversion, etc., and further fails to interpret the Beckmann reaction as applied to the benzil dioximes. The new theory proposed by A. depends essentially on the existence of a generally unstable modification (=C:N(:O)H, "nitrone") containing quinquevalent N, intermediate between the 2 usually stable isomers (=C:NOH, "oxime," and =C(O)—NH, "isoöxime") containing tervalent N. While the last 2 represent groups of sufficient stability to enable compds. containing them to be isolated in the free state, it would be expected that in suitable circumstances there would be a possibility of isolating the 3rd isomeric oxime having the "nitrone" formula. An explanation, using this theory, is made of the number of isomerides known to exist, the difference in the salt-forming properties of the oxime groups present in isomeric oximes, and the formation of *O-* and *N*-ethers, resp., from isomeric oximes. II. **A fourth benzil dioxime.** FREDERICK WM. ATACK AND LEONARD WHINYATES. *Ibid* 1184–8. —*δ-Benzil dioxime* is prepd. by dissolving 0.5 g. α-benzil dioxime in 20 cc. cold NaOH, allowing it to stand 2 hrs., dilg. with an equal vol. H_2O and adding NH_4Cl. The powder m. 217°. If the reaction product of $NH_2OH.HCl$ upon α-benzil monoxime in NaOH soln. is pptd. with NH_4Cl, the new isomer is also obtained. The δ-isomer is characterized by the formation of a buff-colored *nickel compound* on the addition of an NH_4OH soln. of a Ni salt to the NaOH soln. It differs by the facility with which it passes into the red Ni compd. of α-benzil dioxime. The δ-isomer is unstable in solvents, and passes rapidly in alc. in the presence of acids or NH_3 into the α-isomer. C. J. WEST

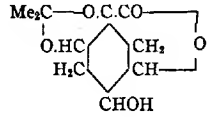
The solubility of phthalic acid in water and sodium sulfate solutions. L. MCMASTER, E. BENDER AND E. WEIL. *J. Am. Chem. Soc.* **43**, 1205–7(1921).—The soly. of phthalic acid, in g. per 100 g. of satd. soln., in H_2O, 10% and 15% Na_2SO_4, resp., at different temps. is as follows: 25°, 0.7014, 0.6440, 0.5272; 35°, 1.0125, 0.9338, 0.7575; 45°, 1.446, 1.341, 1.080; 55°, 2.168, 1.858, 1.639; 65°, 3.246, 3.018, 2.455; 75°, 4.926, 4.373, 3.748; 85°, 7.687, 6.461, 5.533. CHAS. A. ROUILLER

Isomerism of ethyl formylphenylacetate. VI. Alkylation of ethyl formylphenylacetate. WILHELM WISLICENUS AND ROBERT V. SCHRÖTTER. Univ. Tübingen. *Ann.* **424**, 215–32(1921); cf. *C. A.* **15**, 503.—The action of methylating agents upon $HCOCHPhCO_2Et$ (A) gives a mixt. of *ethyl methoxymethylenephenylacetate*, $MeOCH{:}CPhCO_2Et$ (B) and *ethyl α,α-formylphenylpropionate*, $HCOCMePhCO_2Et$ (C). The two forms may be sepd. by distn., since B boils considerably higher. The action of 13.5 g. MeI upon 20 g. of the Na compd. of A gave approx. 9.5 g. C and 0.7 g. B. If the reaction is carried out in a sealed tube at 120°, the total yield is slightly smaller, but C is the principal product. 15 g. A in 52.5 g. 10% NaOH and 10 g. Me_2SO_4 gave 1.5 g. C and 10 g. B. When A was dissolved in Me_2SO_4 and a concd. soln. of 3.2 g. NaOH added, the proportions were about the same (1.5 g. C and 11.2 g. B). The reaction at a higher temp. leads to *ethyl α-phenylpropionate*, $MeCHPhCO_2Et$, b.

229–30°. When the Na compd. of A is suspended in C_6H_6 and treated at the boiling temp. with Me_2SO_4 about equal amts. of B and C are formed. B, b_{15} 173–5°, prisms or needles, m. 54–5°. It decolorizes $KMnO_4$ and adds 2 atoms. Br, which is quant. split off when a $CHCl_3$ soln. is concd. in vacuum. B is stable at 200° but when heated 24 hrs. at 240° it gives C. C, b_{15} 125–7°, has a fruit-like odor, does not add Br, and does not decolorize $KMnO_4$. It does react with fuchsin-H_2SO_3. The action of $PhNHNH_2$ at 190° gives *1,4-diphenyl-4-methyl-5-pyrazolone*, pale yellow prisms, m. 57°. C reacts very slowly, and gives a small yield (1.4%). With EtONa C gives $PhCH_2CO_2H$, and B yields $PhCHMeCO_2H$. The two compds. are fairly stable towards dil. H_2SO_4; C gives $PhCH_2CHO$, while B gives a small amt. of an oily aldehyde, b. 203–5°, which gives a hydrazone, m. 128–9° ($PhCHMeCHO$?). *Ethyl ethoxymethylenephenylacetate*, $EtOCH{:}CPhCO_2Et$, b_{12} 174–7°, results in small yields by the action of EtI on the Na compd. of A and in much larger yields by the action of Et_2SO_4 upon A. This has the same properties as B. *Ethyl formylethylphenylacetate*, $EtC(CHO)PhCO_2Et$, b_{12} 125–7°, results in larger yields by the use of EtI than with Et_2SO_4. *Ethyl formylbenzylphenylphenylacetate*, $PhC(CHO)(CH_2Ph)CO_2Et$, by the action of $PhCH_2Cl$ upon the Na compd. of A, b_{17} 184–5°. A small amt. of the benzyl ether of the enolic form is also formed. *Ethyl α,α-formylphenylsuccinate*, $PhC(CHO)(CO_2Et)CH_2CO_2Et$, by the action of $BrCH_2CO_2Et$ upon the Na compd. of A, b_{12} 203–5°; yield 51%. *Ethyl carbethoxymethylenephenylacetate*, $EtO_2COCH{:}CPhCO_2Et$, by shaking the Na compd. of A with $ClCO_2Et$, b_{15} 199°; yield 69%. C. J. WEST

New derivatives of quinic acid. HERMANN O. L. FISCHER. Univ. Berlin. *Ber.* 54B, 775–84(1921).—Tetraacetylquinic acid, prepd. by the method of Erwig and Königs (*Ber.* 22, 1457(1889)) except that the Ac_2O is removed by distn. *in vacuo* and the product is crystd. from Et_2O and petr. ether, seps. with 1 mol. Et_2O; 20 g. of this acid in 100 cc. $CHCl_3$ treated with 58 g. PCl_5, poured off from the unused PCl_5, freed from the $CHCl_3$ and $POCl_3$ as completely as possible with the H_2O pump, taken up in 25 cc. warm $CHCl_3$ and treated with 100 cc. Et_2O and then with 80–90 cc. petr. ether to incipient turbidity gives 70 g. *tetraacetylquinyl chloride*, microprisms, begins to sinter 104°, and changes to a viscous mass becoming clear and mobile at 122°, quickly dissolves in hot MeOH and on cooling yields the Me ester, decomps. on long standing, even *in vacuo* over P_2O_5, evolving the odor of AcCl. *Anilide*, obtained in 72% yield from the chloride in $CHCl_3$ dropped into 2 mols. $PhNH_2$ in Et_2O, m. 211–2°. *Azide* (6 g. from 2.6 g. NaN_3 in 20 cc. freezing H_2O treated with 15 g. of the chloride in 40–5 cc. Me_2CO, poured after 5–7 min. into 300–400 cc. H_2O, taken up in Et_2O, cautiously evapd. *in vacuo* and crystd. from 12 cc. MeOH at −15°), decomps. 93–5°, deflagrates when heated on Pt foil; 7 g. in 5 cc. PhMe heated on the H_2O bath until no more gas is evolved decomps. into N_2, CO_2, AcOH and 3.4 g. *p*-$AcNHC_6H_4OAc$. From 25 g. powdered and bolted quinic acid shaken 2–3 days at room temp. with 500 cc. Me_2CO containing 1% HCl, filtered from the undissolved portion (6–8 g.), shaken 1 hr. with $PbCO_3$, filtered, evapd. *in vacuo* at 30–5° and crystd. from AcOEt-petr. ether is obtained 75% of *acetonequinide* (A), fine needles, m. 140–1°, $[\alpha]_D^{18}$ −36.65° in $(CHCl_3)_2$, mol. wt. in freezing AcOH 238–47; 10 g. quickly dissolved in 100 cc. of 0.1 *N* HCl at 50°, kept 30 min. longer at this temp.; freed from HCl by shaking with an excess of Ag_2CO_3, evapd. *in vacuo* at 35–40°, extd. 3 times with 75 cc. boiling alc. and concd. to 15–20 cc. gives 4.5 g. quinide (B), sinters about 172°, m. 187° and, contrary to Hesse's prepn. (*Ann.* 110, 336(1859)), is optically active, $[\alpha]_D^{16}$ −17.08° (H_2O). If Erwig and Königs' formula for quinic acid is accepted and the lactone formation is assumed to occur in the γ-position A would have the structure I, but F.'s observations are not in conflict with Emde's formula (*C. A.* 12, 2543); if this is correct, A would have the structure II. B (2 g.) allowed to stand 20 hrs. with 2 cc. each of C_5H_5N and Ac_2O and poured into 50 cc. AcOH

yields 80% *triacetylquinide*, prisms from Me_2CO–H_2O, m. 134–5°, $[\alpha]_D^{15}$ −13.23° (Me_2CO). *Methylacetonequinide*, $C_{11}H_{16}O_5$ (2 g. from 3 g. A, freshly crystd. from H_2O and dried over P_2O_5, dissolved under a reflux in 80 cc. boiling Et_2O and 40 g. MeI, then treated in the course of 1 hr. with 13 g. freshly pptd., dry Ag_2O, boiled 6–7 hrs. under a reflux), filtered and freed from the Et_2O-MeI on the H_2O bath and finally at 50–60° *in vacuo*, elongated prisms from ligroin, sinters 76°, m. 78–9°, $[\alpha]_D^{23}$ 10.28°. In an attempt to replace the free HO group in A by Cl by Darzen's method (*C. A.* **5**, 3410) 5 g. A in 4 cc. cold C_5H_5N was treated with 1.4 g. $SOCl_2$, slowly heated to 115°, kept 15 min. at this temp., treated with H_2O, extd. with much Et_2O, shaken several times with dil. H_2SO_4 and dried with Na_2SO_4; there was thus obtained 4 g. of a compd., $C_{20}H_{28}O_{11}S$, needles from CCl_4, m. 104–5°, mol. wt. in freezing $CHBr_3$ 454, which is apparently *bis*[*acetonequinide*] *sulfite*.



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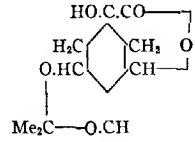


II

CHAS. A. ROUILLER

Acid constituents of maritime pine gum. Isomerization of the pimaric acids. GEORGES DUPONT. *Compt. rend.* **172**, 1373–5(1921); cf. *C. A.* **15**, 2434.—Abietic acid, the principal constituent of various resins, is a mixt. of complex isomorphous acids produced by the action of heat on the pimaric and the sapinic acids. This paper reports the results of a study of the isomerization of *d*- and *l*-pimaric acids by the catalytic action of HCl. *d*-Pimaric acid treated with 1% HCl at 13° showed no change in rotatory power, $[\alpha]_J$ −63.5°, during a period of 10 days. *l*-Pimaric acid under the same conditions showed the following changes in $[\alpha]_J$: initial −282.4°, after 10 min. −254.8°, 1 hr. −204.2°, 9.5 hrs. −79.0°, 24 hrs. −76.4°, 31.5 hrs. −77.8°, 176 hrs. −91.6°, 242.6 hrs. −94.2°. These figures show that the action takes place in 2 stages; first stage, the transformation of the acid into an unstable isomer with $[\alpha]_J$ −76.4°, $[\alpha]_V$ −87.6 and $[\alpha]_I$ −163.2; J, V and I signifying yellow, green and violet lines of the Hg arc. The cryst. form of this substance is named *α-pimarabietic acid*. That this action is catalytic is indicated by conformity to the law of mass action, $[\alpha]_o$ being the

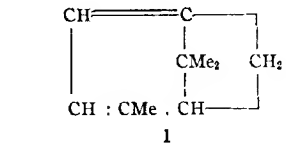
$$K = \frac{1}{t - t_o} \log \frac{[\alpha]_o + 76.4}{[\alpha] + 76.4}$$

rotatory power at the instant t_o and $[\alpha]$ at the instant t. K is a const. which verifies this formula when $K = 0.00288$, and which is proportional to the concn. of the catalyzer. In the second stage the α-pimarabietic acid is further transformed under the same conditions that existed during its formation, into a substance which crystd. from alc., m. 172–3°, $[\alpha]$ −100.1°, $[\alpha]_V$ −115.4. This substance appears to be identical with that of Schultz (*C. A.* **12**, 1297) and is named *β-pimarabietic acid*. AcOH in place of HCl produces a slow isomerism in the cold, rapid and complete in 40 min. at 100°. Also in *Bull. soc. chim.* **29**, 727–36(1921).

L. W. R.

Verbenene (dehydro-α-pinene) and some of its derivatives. A. BLUMANN AND O. ZEITSCHEL. Anton Deppe Söhne, Hamburg-Billbrook. *Ber.* **54B**, 887–94(1921); cf. *C. A.* **7**, 2564.—From 1.34 g. verbenene (I) in cold $CHCl_3$ treated with N Br unti the Br color persists (20.8 cc.) is obtained the *d-dibromide* (II), prisms from petr. ether

m. 70–2°, darkens, liquefies and gives off HBr on standing, is not attacked by $KMnO_4$ in H_2O or Me_2CO, $[\alpha]_D^{15}$ 297.65 (C_6H_6). *l-Dibromide*, from *d*-verbenene, m. 70–2°, $[\alpha]_D^{18}$ −298.50°. *dl-Isomer*, from equal amts. of the antipodes, needles from ligroin, m. 50–2°. When 5.9 g. II are shaken 15 hrs. with 200 cc. of 2% KOH, the Br atoms are replaced by HO and at the same time there seps. 1.7 g. of an oxide-like *compound* (III), oil, d_{15} 0.997, α_D in 10% alc. soln. in a 50-mm. tube −4.50°; the mother liquors, extd. with petr. ether, yield 0.9 g. of the *glycol*, prisms from H_2O, m. 141°. The *d*-bromide (10 g.) in 100 g. AcOH and a few drops H_2O slowly treated in the cold with 22 g. Zn dust and shaken 1 hr. gives 3.7 g. pure I, b_{11} 45°, b_{745} 158–9°, d_{15} 0.8866, $[\alpha]_D$ −100.61°. *d*-I from the *l*-dibromide, d_{15} 0.8867, $[\alpha]_D$ 100.71, n_D^{20} 1.49800. Pure I (3 g.) shaken at room temp. with 18 g. $KMnO_4$ and 6 g. KOH in 600 cc. H_2O until the $KMnO_4$ is decolorized (about 45 min.), gives *cis*-norpinic acid, m. 175.5–6.5°. From 3 g. I boiled a few min. with 0.5 g. $ZnCl_2$ and distd. with steam is obtained 1.2 g. volatile products which, treated with dil. $KMnO_4$ until the color persists and further oxidized with boiling $KMnO_4$, yields 0.8 g. *p*-$Me_2C(OH)C_6H_4CO_2H$, m. 156–7°. *l*-I (20 g.) in 100 g. alc. reduced with 10 g. Na, treated with H_2O, distd. with steam and put through the same process (3–4 times) until the rotation no longer changes yields 15 g. *dihydroverbenene* (IV), oil with pronounced pinene odor, b_{762} 158–9°, d_{15} 0.865, d_{20} 0.8625, n_D^{20} 1.4662, $[\alpha]_D$ 36.52°, adds Br but without showing any sharp end-point and the resulting bromide does not solidify; 5 g. yields by Wallach's method only 0.5 g. of a *nitrosochloride*, m. 103–4°, converted by NaOEt into nitrosopinene, m. 131–2°. IV (5 g.) in 10 g. cold CS_2 satd. with dry HCl gives 1.7 g. pinene-HCl, m. 130°, while 3 g. shaken 24 hrs. with 100 cc. of 10% H_2SO_4 yields 1.4 g. *cis*-terpinol hydrate, m. 117°.



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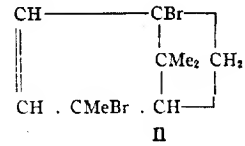

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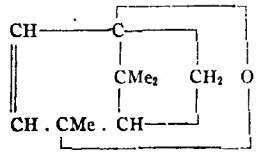

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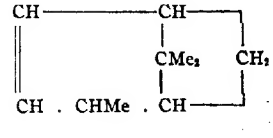
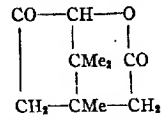


IV

CHAS. A. ROUILLER

Epicamphor. II. WILLIAM HENRY PERKIN, JR., AND ALAN FRANCIS TITLEY. Univ. Oxford. *J. Chem. Soc.* **119**, 1089–1107(1921); cf. *C. A.* **6**, 2598.—*Hydroxymethylene-l-epicamphor*, $C_{11}H_{16}O_2$, is prepd. by adding 13 g. *l*-epicamphor in Et_2O to 3 g. granular Na and then adding 17 g. iso-AmO_2CH and allowing the mixt. to stand 24 hrs. The product is poured into ice H_2O, extd. with Et_2O, acidified with AcOH and the solid product distd. with steam, when it m. 89°, has a faint odor, is slightly sol. in hot H_2O, has $[\alpha]_D$ in C_6H_6 = 124.5°, and shows a slight mutarotation as compared with the camphor deriv. A 3-weeks-old specimen in alc. showed $[\alpha]_D$ −138.8°. The alc. soln. gives a violet color with $FeCl_3$ and reduces Ag_2O. *Benzoate*, $C_{18}H_{18}O_3$, glittering plates, m. 105–6°. *Semicarbazone*, $C_{12}H_{19}O_2N_3$, very small needles, decomp. 196–7°. *Anilinomethylene-epicamphor*, small, faintly yellow needles, m. 101°, $[\alpha]_D$ −271.5°; it does not

show an appreciable mutarotation. *β-Naphthylaminomethylene-epicamphor*, $C_{21}H_{23}ON$, pale yellow, silky needles, m. 109–10°. The C_6H_6 soln. showed $[\alpha]_D$ −202.5°, which increased to 222.5° in 24 hrs. and showed no further change. Heated with aq. NH_4OH in a sealed tube at 100° for 4–5 hrs., *aminomethylene-epicamphor*, $C_{11}H_{17}ON$, is formed, needles, m. 122°, $[\alpha]_D$ −296.9°. The camphor deriv. showed a change in $[\alpha]_D$ from 300.8° to 228.3° in 24 hrs. and to 218.6° in 1 week. *l-Epicampholenonitrile*, $C_{10}H_{15}N$, was prepd. by heating the oxime with 20% H_2SO_4 for 2–3 hrs. on the H_2O-bath, b_{100} 145°, b_{764} 214°, $[\alpha]_D$ −27.4° in AcOEt, d_{15} 0.921, n_D 1.4732. The *derivative* b_{100} 146–7°. The nitrile is very difficultly hydrolyzed and must be heated 10 days in a sealed tube at 100° with a large excess of MeOH-NaOH. *l-Epicampholenic acid* (A), rather viscous oil, b_{10} 166°, b_{100} 181°, $[\alpha]_D$ −38.4° in AcOEt. The *d-acid* b_{10} 164–5°, $[\alpha]_D$ 39.2°. The neutral oil obtained from the acid is probably *dihydroepicampholenolactone*, $C_{10}H_{16}O_2$, b_{10} about 168°, $[\alpha]_D$ −3.47°. *l-α-Campholenonitrile*, b_{100} 153°. *l-α-Campholenic acid*, b_{10} 155°. *dl-Acid*, b_{40} 169°. *l-Epicamphylamine*, $C_{10}H_{19}N$, by reducing the nitrile with EtONa, b_{100} 127–8°, $[\alpha]_D$ 17.6°. It absorbs CO_2 from the air, forming a solid carbonate. The oxidation of A by $KMnO_4$ gave the *lactone of hydroxyketodihydroepicampholenic acid*,

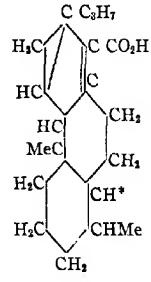


long needles, m. 80°, volatile with steam, sol. in alkalies, $[\alpha]_D$ 45.8° in AcOEt. The other product is an *acid*, $[\alpha]_D$ 190.1°, the *ethyl ester* of which b_{10} 150–5°, and has $[\alpha]_D$ 34.4°. The liberated acid gave a *semicarbazone*, $C_{11}H_{19}O_3N_3$, m. 202–3°. Upon further oxidation with $KMnO_4$, a *diketo acid* is formed, the *ethyl ester* of which, $C_{12}H_{18}O_4$, b_{30} 183–5° and the *semicarbazone* of which, $C_{11}H_{17}O_4N_3$, m. 168°. C. J. West

Pinabietic acid, a homogeneous resin acid. I. Occurrence and purification of the acid. Ossian Aschan. Univ. Helsingfors. *Ann.* **424**, 117–33(1921).—This work grew out of an effort more economically to utilize rosin and alum in the sizing of paper. The raw material consisted of the difficultly volatile part of the so-called "pine oil," after being freed from fatty acids and other volatile acids by the method of Hellström (*Tekn. Fören. Förk.* 1916, 216). This consists of a powdery, yellowish fine crystal meal, mixed with a darker molasses-like material and brown lumps. The latter is sepd. mechanically and the remainder dissolved in about its own wt. of commercial MeOH (98%) by boiling and the filtered soln. held at room temp. for about 4 hrs. The pinabietic acid (150 g. from 500 g. crude material), after washing with MeOH, m. 160°. This was then heated with 10% excess of Na_2CO_3 soln. until soln. resulted and CO_2 run in until no further ppt. formed, and the acid liberated by boiling with 96% EtOH and AcOH. Finally the product was crystd. from AcOH and then from 98% MeOH. Yield, 10%. *Pinabietic acid*, $C_{20}H_{30}O_2$, small prisms, m. 182–3°. Like all resin acids, it has a tendency to adsorb different compds. from solns. Thus A. glistening leaflets were obtained, m. 161–2°, which seemed to be a pure compd. The mother-liquors gave glass-glistening plates, m. 170–2°, the m. p. of which remained const. through several crystns. from alc. That these were mixts. followed from the rotations. This purification may be followed under the microscope. The pure acid is insol. in H_2O, and nearly insol. in petr. ether and ligroin. It is easily sol. in C_6H_6, Et_2O, $CHCl_3$, CS_2, Me_2CO, AcOEt, etc. It is stable when heated in absence of air and may be distd. *in vacuo*. It is slowly decompd. when heated in air. After 1 yr. the m. p. had decreased 2°. *Sodium salt*, $C_{20}H_{29}O_2Na$, by adding the calcd. amt. of Na_2CO_3 to a MeOH soln., needles which are not soap-like. Easily sol. in H_2O, Na_2CO_3 ppts. it in cryst. flakes.

The *double salt*, $C_{20}H_{29}O_2Na.3C_{20}H_{30}O_2$, ppts. when CO_2 is passed into a soln. of the normal salt and forms a hard mass with a glistening surface, which gives a colloidal soln. in H_2O. This may be used for the sizing of paper. Crystd. from a small amt. hot EtOH the *salt* $C_{20}H_{29}O_2Na.2C_{20}H_{30}O_2$ seps. Oxidation of the free acid in Me_2CO with $KMnO_4$ gave a mixt., from which only the unchanged acid could be isolated. Attempts to form a glyceride by heating 1.5 g. $C_3H_5(OH)_3$ with 4.6 g. acid in an evacuated flask at 200–230° for 21 hrs. gave a mixt. Attempts to add AcOH with an opening up of the $CH_2:CH_2$ linking according to Bertram-Walbaum likewise gave a mixt which could not be purified. The acid adds HCl in MeOH soln., but does not in Et_2O. The acid shows the same color reactions as abietic acid (Mach, *Monatsh.* **15**, 631) with $CHCl_3$, AcOH and H_2SO_4, and with HCl and $FeCl_3$, but when dissolved in concd. H_2SO_4 the color is yellow (instead of red) and upon shaking with $CHCl_3$ the $CHCl_3$ is colorless (instead of red), and when heated with HNO_3 and moistened with NH_3 the color is orange-yellow and not red. II. **Molecular weight and rotation of pinabietic acid.** Ossian Aschan and K. E. Ekholm. *Ibid* 133–50.—The mol. wt., using Et_2O as a solvent, was found by the b. p. method to be 302.7; titration in alc. with phenolphthalein gave 302.1, 300.8, 301.2, 300.4, thus clearly indicating the formula $C_{20}H_{30}O_2$. The acid is characteristic in that it has a positive rotation in solns. of aromatic hydrocarbons, and a negative rotation in solns. of alcs., etc. The following values were found for $[\alpha]_D$: C_6H_6, 21.3; C_7H_8, 21.8; *m*-$C_6H_4Me_2$, 25.68; *p*-cymene, 16.1; 1,3,5-$C_6H_3Me_3$, 8.84; petr. ether, −14.53; ether, −30.6; Me_2CO, −19.17; $CHCl_3$, −20.05; AcOEt, −23.35; MeOH, −29.47; abs. EtOH, −30.76. The addition of abs. alc. to a C_6H_6 soln. changed the sign of the rotation; the zero point was at about 92% C_6H_6. There are indications that in the compd. or mixt. m. 167.5–9.5°, a 2nd abietic acid is present, which has a positive rotation in both C_6H_6 and alc. Only ordinary abietic acid could be isolated from the resin of *Pinus silvestris*. III. **The constitution of pinabietic acid.** Arturi I. Virtanen. *Ibid* 150–251.—*Silver pinabietate*, amorphous, easily sol. in Et_2O. *Calcium salt*, small needles. *Barium salt*, glistening needles with 1 H_2O, sol. in alc., insol. in Et_2O. *Lead salt*, small needles, m. about 140°. *Strontium salt*, needles with 7 H_2O. *Copper salt*, long, dark blue needles. *Methyl ester*, $C_{21}H_{32}O_2$, by the action of Me_2SO_4 on the Na salt in NaOH, yellow oil, b_{16} 225–6°, d_4^{21} 1.0500; n_D^{21} 1.52685; M_D 92,582. *Ethyl ester*, $C_{22}H_{34}O_2$, from the Ag salt and EtI, nearly colorless oil, b_{20} 241–2°, d_4^{21} 1.0339, n_D^{21} 1.52129, M_D 97,320. These esters are difficultly sapond. The following figures are the values for $[\alpha]_D$ at 20–23° for the Et and the Me esters, resp.: C_6H_6, 12.48, 14.85; C_7H_8, 11.23, 13.97; cymene, −, 7.14; abs. alc., −7.77, −4.36; abs. MeOH, −7.91, −4.71; Et_2O, −8.15, −3.66; $CHCl_3$, −, 5.94. They thus show the same characteristic as the free acid. *Chloride*, a thick, sticky mass which could not be purified. The amide was obtained amorphous only. *Dihydrobromopinabietic acid*, $C_{20}H_{32}Br_2O_2$, by treating 12 g. of the acid in 190 g. AcOH with an excess of AcOH-HBr, fine needles, decomp. 188–92°. The action of HI appears to give a *hydroiodopinabietic acid*, m. 191–3°. *Dibromopinabietic acid*, by the action of Br in CS_2 on the acid, glistening needles, m. 107–10°. The I no., detd. according to Hübl, indicated the presence of 2 double bonds. *Dihydropinabietic acid*, by reducing with H and Pt black in AcOH, small, quadratic needles, m. 170–5°. Distn. of the acid with S gave retene, $C_{18}H_{18}$. From the oxidation of the acid with CrO_3 only AcOH could be isolated; $KMnO_4$ in alk. soln. gave as the only isolated compd. Me_2CHCO_2H. No better results were obtained with O_2 and HNO_3. *Dinitropinabietic acid*, $C_{20}H_{28}N_2O_6$, by the action of 1.52 HNO_3 cooled in ice-salt mixt., small needles or prisms, m. 190–3°, which become a dirty green in the light; $[\alpha]_D^{22}$ 43.89 in Me_2CO. *Ammonium salt*, needles. *Sodium salt*, flat needles, very sensitive to light. *Silver salt*, small needles. *Methyl ester*, by the action of HCl upon an alc. soln. or from the Na salt and Me_2SO_4, m. 180–3°.

Ethyl ester, $C_{22}H_{32}O_6N_2$, from the Ag salt and EtI, glistening needles, m. 160–2°, $[\alpha]_D^{23}$ in Me_2CO, 42.03. Upon reduction both NO_2 groups are changed to NH_2, but a pure product could not be prepd. The amorphous chloride upon distn. *in vacuo* splits off HCl and CO and yields *pinabietin*, $C_{19}H_{28}$, also obtained by heating the acid in a sealed tube at 260–70°, b_{10} 191–4°, d_4^{20} 0.9734. It does not yield a picrate. It is stable towards $KMnO_4$. However, it adds 4(?) atoms. Br and also HCl, though pure products were probably not obtained. With H_2SO_4 it gives a *monosulfonic acid*, isolated as the impure *calcium salt*, $(C_{19}H_{27}SO_3)_2Ca$. HNO_3 gave a mixt. of several NO_2 derivs. Heated with S, retene was formed. Oxidized with HNO_3, a very small yield of 1,3,4-$C_6H_3(CO_2H)_3$ was isolated. MnO_2 and H_2SO_4 gave a better yield of the same acid. The abietic acid of Johansson (*C. A.* **12**, 583) is identical with pinabietic acid. A consideration of the above reactions and properties leads to the following suggested formula for the acid (the Me group might also be bound to the C which is starred):



C. J. West

New constituents of colophony, the colophenic acids and analogs. Ossian Aschan. Univ. Helsingfors. *Ber.* **54B**, 867–86(1921); cf. *Finska Kem. Med.* **26**, 70(1917). —In the course of the investigation of pinabietic acid (see preceding abstr.) A. found in the same crude material several acid constituents which are of special interest in that they are present in American as well as Finnish com. colophonies. The acids of the general compn. $C_nH_{2n-10}O_4$ are designated *colophenic acids*. They are accompanied in colophony by other acids differing from them in degree of satn. and in O content. Insofar as it has been possible to isolate them in homogeneous form, these colophenic acids differ from the resin acids in that, though being monobasic, they contain 4 atoms of O; moreover, they are peculiar in that the solns. of their alkali salts, which foam but little like soaps, are dark yellow to brownish yellow while the free acids in pure form show only a faint yellowish tinge. The dark alk. solns. cannot be decolorized with charcoal; the colophenic acid mols. are, therefore, chromogenic in character. Although they react with $PhNHNH_2$, it has not yet been possible to establish their ketone nature. With ammoniacal Ag solns. they give, even on heating, stable Ag salts, so that they are not aldehyde acids. Neither are they lactones, for on heating with 0.1 *N* KOH they take up only 1 mol. alkali. On the other hand they seem to contain a HO group. The dark color of the paper manufacturer's *Leimgalle* (the ppt. which forms upon boiling rosin size soln.) is probably due to the presence of these acids, for A. has succeeded in isolating from such a *Leimgalle* a substance behaving like a colophenic acid. Their thorough study should be of interest for the com. prepn. of colophony for it is doubtless they which, in great part at least, impart color to the different kinds of colophony and if methods of removing them can be devized it might be possible to make the cheaper, dark colophonies better adapted for sizing. They easily dissolve all sorts of substances and as they are amorphous and

low melting, they probably exercize an influence on the glassy consistency of colophony which protects it from oxidation by the air. They cling to the resin acids with extreme tenacity and they are probably responsible for the fact that Mach (*Monatsh.* **15**, 627 (1894)) and Easterfield and Bagley (*J. Chem. Soc.* **85**, 1238(1904)) found for ordinary abietic acid and A. himself at first for pinabietic acid analytical values agreeing better with the formula $C_{19}H_{28}O_2$ than with $C_{20}H_{30}O_2$; the too low m. ps. generally found for the abietic acids are doubtless due to traces of the colophenic acids. As they are somewhat sol. in H_2O, they are probably present in beer, especially of the poorer kinds, to which they impart a bitter taste; the typical bitter taste of colophony is also without doubt due to them. They are easily sol. in all org. solvents except petr. ether. They differ sharply from the resin acids in the easy soly. of their Na salts in cold H_2O and in the stability of these salts towards CO_2; while moist, as obtained by evapn. of the aq. or alc. solns. they are soap-like and when dry are yellowish white, non-hygroscopic and stable in the air. The Ba and Ca salts are relatively easily sol. in much H_2O and are pptd. by $BaCl_2$ or $CaCl_2$ from solns. of the NH_4 salt which, when concd., form thick sols; the Ag and Cu salts yield somewhat turbid, probably colloidal solns. with H_2O. The acids are highly unsatd. and instantly decolorize $KMnO_4$. They instantly dissolve in HNO_3 (d. 1.48) with strong evolution of heat and unless strongly cooled liberate N oxides violently. The cold brown soln. poured upon ice gives a ppt. of yellow, partly cryst. flocks sol. in soda and NH_3 with red-orange-yellow color. Concd. H_2SO_4 dissolves the acids with reddish yellow color which soon becomes almost blood-red and is stable for a long time. With the Mach reagent for abietic acid they give a very transient red color (often visible for only a moment), changing, without passing through a blue, to a faint violet and finally a brownish green; probably they, as well as the resin acids, are analogous in structure to cholesterol. A similar analogy between the three classes of compds. is shown by evapg. them on a watch glass with $FeCl_3$ and concd. HCl, the colophenic acids yielding a red ring and the solid particles remaining as dark greenish brown masses. Whether these colophenic acids are already present, preformed, in the oozing resin or are formed later by the action of the air, cannot be detd. at present. In this connection it is of interest that one at least has been obtained in up to 25% yield by treating Na pinabietate with H_2O_2 on the H_2O bath, and under conditions which have not yet been fully established they may also be obtained by the action of free O on the resin acids at a low temp. In view of the totally unknown nature of their inner structure a very general principle must be followed for the present in naming them, and A. uses the number of C atoms they contain in designating them; thus, $C_{16}H_{28}O_4$ is called hexadecacolophenic acid. The identification of all these acids is very difficult as, on account of their amorphous nature, they soften or melt only very gradually. The crude material for a part of this work was obtained by distn. with superheated steam of the so-called pine oil which is formed when the rosin soaps sepg. from the black lye of sulfate-cellulose manuf. are pptd. with H_2SO_4 or $NaHSO_4$. On standing the oily distillate deposits large yellow to yellow-brown lumps which are sepd. from the oily portion. On rubbing with MeOH, the outside of these lumps dissolves almost completely, leaving the core of pinabietic acid largely undissolved. The sirupy residue remaining on evapg. the MeOH ext. is dissolved in boiling 1% Na_2CO_3, cooled, treated with NaCl to ppt. the crude Na pinabietate (which is washed with concd. NaCl until the washings are no longer colored) and the combined filtrates treated with dil. H_2SO_4; the voluminous ppt., which soon becomes granular, is again dissolved in dil. soda, treated in the dark with CO_2 until no further ppt. of resinate is formed, filtered and pptd. with HCl in slight excess; this process is repeated at least twice and the product is washed with cold H_2O until free from Cl and dried *in vacuo*. For the sepn. of the acids from various kinds of colophony either the above or one of the two following methods

can be used. (1) 100 g. colophony (calcd. as $C_{20}H_{30}O_2$) is heated almost to boiling with 1.1 equiv. Na_2CO_3 in 1 l. H_2O until no more dissolves, cooled, treated with washed CO_2 as long as a ppt. or turbidity is produced (about 6 hrs.), filtered, treated with HCl (about d. 1.12) to distinct acid taste and again dissolved in soda and cautiously pptd. (2) 100 g. powdered colophony, 1 equiv. calcined soda and 2 l. H_2O are boiled until (colloidal) soln. results, treated hot with 32 g. NaCl, cooled, filtered, again treated with 13 g. NaCl, then with CO_2 for 5 hrs., filtered and pptd. as above with HCl. The yields of crude colophenic acids from different colophonies ranged from 2 to 10%. The true colophenic acids are sol. in cold C_6H_6 while a part of the accompanying acids is often insol. even in hot C_6H_6; the crude mixt. is heated with about 10 parts C_6H_6, the soln. concd. to 0.5 its vol. and pptd. with petr. ether. After they have thus been sepd. into three fractions, they are freed from the tenaciously adhering C_6H_6 or petr. ether by immediately dissolving in soda, boiling out the org. solvent and pptg. with HCl. The *hexadecacolophenic acid* obtained from the pine oil from the black lye exists in 2 forms, large yellow granules when pptd. from concd. solns. of the Na salt, and an almost colorless powder with yellowish tinge from more dil. solns. They m. 96–105° and 86–98°, resp., and evolve gas at 128–30° (probably H_2O, for even after heating 0.5 hr. at 250° and then dissolving in soda it is pptd. unchanged by HCl). The two forms can be changed into each other at will by changing the conditions of pptn. *Silver salt*, grayish reddish yellow. In C_6H_6 the acid shows $[\alpha]_D^{17}$ 21.66–22.33°. With $PhNHNH_2$ in AcOH it forms after a time a dark resinous ppt. Boiled 8 hrs. with 4 parts Ac_2O and 2 parts NaOAc it yields a product, the titration of which before and after hydrolysis indicates that it is a *monoacetate*, sol. in soda with the same dark color as the original acid. From 2 samples of American colophony was obtained a similar acid in 5% yield, also by treating 2 g. pinabietic acid in 1.25 equivs. soda and enough H_2O for soln. with 8 mols. H_2O_2 on the H_2O bath until no more O was evolved. In the last case, there remained in the C_6H_6-petr. ether mother liquors another acid, *dehydroeicosicolophenic acid*, $C_{20}H_{28}O_4$(?), almost white powder, sinters 70°, m. 85–8°, sol. in alkalies with brownish yellow color, gives with the Mach reagent a crimson color changing directly to yellow-brown, sol. in concd. H_2SO_4 with bright orange-yellow color, has a less bitter taste than colophenic acid. A Finnish colophony yielded a *heptadecacolophenic acid*, faintly yellowish white powder, sinters 70–5°, m. 100–5°, gives a strong blood-red color with H_2SO_4 and a positive Mach test, and also small amts. of two other *acids*, $C_{12}H_{18}O_4$, $C_{18}H_{32}O_4$ or $C_{13}H_{24}O_6$, one of which sinters 85–90°, m. completely about 150°, and the other sinters 60°, m. 65°. From a sample of *Leimgalle* from American colophony were obtained an *octadecacolophenic acid*, light yellowish white, bitter powder, sinters 105–10°, m. 180–4°, sol. in H_2SO_4 with bright yellow color changing to red-orange, a very bitter *acid* $C_{13}H_{18}O_4$, sinters 95–100°, m. 105–10°, and a small amt. of an *acid* $C_{13}H_{24}O_2$, sinters 70–5°, m. 85–7°. *Eicosicolophenic acid*, obtained from two dark brown samples of American colophony, very bitter, sinters 80–90°, m. completely 110°, gives a red color with H_2SO_4 and the Mach reaction; accompanying it were two *acids* whose compn. corresponds best with the formula $C_{18}H_{28}O_3$. CHAS. A. ROUILLER

Crystallographic investigation of *o*-nitroso-*p*-dimethylaminobiphenyl. F. PARDILLO AND M. J. NARANJO. *Publ. Secc. Cienc. Nat. Barcelona* 9, 1920; *Rev. géol.* 1, 378(1920). E. T. WHERRY

The polynuclear phenols of the sodium phenate fusion. FRITZ HOFMANN AND MYRON HEYN. Breslau. *Brennstoff Chem.* 2, 147–50(1921).—Pure PhONa was heated at a const. temp. in an inert atm. The first period of 3–4 hrs. at 150–200° was necessary to remove H_2O; the temp. was slowly raised to 400°, where the melt began to turn brown, and then to 485–490°, where vigorous ebullition took place. The distillate was collected until no more came over, the residue becoming viscous and foamy. 500 g.

PhONa gave about 20 l. of gas analyzing 0.0% CO_2, 0.5% C_2H_4, 1.4% O_2, 0.0% CO, 90% H_2, 8% CH_4 or C_2H_6. The distillate, amounting to 5–8%, contained varying amts., around 80%, of C_6H_6, with some Ph_2 and Ph_2O. The residue was almost completely sol. in 4 times its wt. of H_2O, giving a dark brown soln. On acidification a dark tarry layer sepd. from the aq. soln.; the PhOH, sepd. by Et_2O extn. and distn., amounted to about 20% of the wt. of PhONa used. The pitchy, insol. residue was repeatedly fractionated in a slow CO_2 stream under high vacuum and the fractions were crystd. for further purification. A small yield of *o*-HOC_6H_4Ph was isolated from the lower boiling fractions (about 160° under 1 mm.); the next fractions (about 175–180° under 1 mm.) contained much (*o*-$HOC_6H_4)_2$ m. 109°. The oily mother liquors from this fraction contained a *compound* which gave a bright red color when shaken with NH_4OH in the presence of air. It dissolved in dil. NaOH with a dirty brownish red color. The $FeCl_3$ reaction was first green, then a strongly clouded olive. The fraction b_1 190–230° furnished by crystn. from hot C_6H_6 a new *dihydroxydiphenyl*, crystg. from water in needles, m. 92–3°, giving with $FeCl_3$ in H_2O a bluish violet, in EtOH an olive-green color, much more sol. in hot H_2O than the isomer m. 109°. It is probably 2,3′-dihydroxydiphenyl. In this same fraction and the higher ones, a considerable quantity of (*m*-$HOC_6H_4)_2$ m. 123.5°, was recognized, as well as a small quantity of the 3,4′-isomer, m. 190°. The authors point out the fact that four of the possible six $(HOC_6H_4)_2$ isomers are present in the fusion mixt. The fraction b_1 up to 300° resembled rosin, and could not be crystd. It was completely sol. in dil. NaOH and in C_6H_6, in which its mol. wt. was 295.5. Analysis: C 80.7%, H 5.4%. The authors suggest that it may be *dihydroxytriphenyl*. The pitchy residue was insol. in Et_2O and C_6H_6 but gave colloidal solns. in Me_2CO and C_5H_5N (cf. *C. A.* **15**, 159). W. B. V.

Crystallography of some derivatives of benzophenone. F. M. Jaeger. Groningen. *Z. Krist.* **56**, 46–61(1921).—Ph_2CO itself is well known to be orthorhombic. The 2-NO_2 deriv. is monoclinic; 2-Cl, monoclinic; 2-I, triclinic; 2,4-Br_2, orthorhombic with peculiar optical properties; 2,4′-Br_2, monoclinic; 2-Br and 2,4′-Cl_2, have been previously shown to be monoclinic, and are isomorphous with the corresponding derivs. now described. The 2,4,6-Cl_3 and 2,4,6-Br_3 derivs. have already been described (*C. A.* **2**, 661). The 2-chloro-4′-nitro deriv. is orthorhombic; 2-chloro-4′-amino, monoclinic; 4-chloro-3-nitro, orthorhombic; 4-chloro-4′-nitro, triclinic; 4-bromo-3-nitro, orthorhombic; 4-bromo-3-amino, monoclinic; 4,4′-dibromo-3-nitro, monoclinic, apparently sphenoidal; 3,4′-dinitro-4-bromo, orthorhombic. Several Me derivs. have been described crystallographically; 4-Me is monoclinic, 3,4′-Me_2, monoclinic, 2,5-Me_2, orthorhombic, and 2,4,6-Me_3, orthorhombic bisphenoidal. The 2-bromo-4′-ethoxy deriv. is found to be orthorhombic. These are divisible into 3 groups, there being marked morphotropic relations between members of each group. E. T. Wherry

Combined auxochromes. Hugo Kauffmann. *Ber.* **54B**, 795–802(1921).—The radical PhCH:CH having been shown to have auxochromic properties (*C. A.* **11**, 2805) it became of interest to det. how the introduction of substituents into the radical would influence these properties. As the substituents were chosen groups which are themselves auxochromic (MeO). As the chromogen was used $PhNO_2$ and the substituted styryl radicals were introduced into the *p*-position to the NO_2 group. The following compds. were prepd.: *4′-Methoxy-4-nitrochalcone* (A), $MeOC_6H_4COCH{:}CHC_6H_4NO_2$ (3.4 g. from 2 g. *p*-$O_2NC_6H_4CHO$ and 2.2 g. *p*-$MeOC_6H_4COMe$ in 12 cc. alc. allowed to stand a long time with 10 drops concd. NaOH), light greenish yellow needles from C_6H_6, m. 169°, is colored orange-red by concd. H_2SO_4 and dissolves with orange-yellow halochromic colors. *2′,4′-Dimethoxy-4-nitrochalcone* (B), woolly light yellow needles from C_6H_6, m. 191°, is colored orange-red by H_2SO_4 and dissolves with orange color. *2′,4′-Dimethoxy-4-nitrostilbene* (C) (1.1 g. from 1.9 g. *p*-$O_2NC_6H_4CH_2CO_2H$ and 1.7

g. 2,4-$(MeO)_2C_6H_3CHO$ heated up to 150° with 15 drops piperidine), long brick-red needles from alc., m. 116°, orange-yellow needles from ligroin. *3',4'-Isomer* (D), egg-yellow crystals from alc., m. 133°. *2',5'-Isomer* (E), yellow needles from alc., m. 118°. As is seen by a comparison of the brick-red C with the yellow 4-nitrostilbene, the introduction of 2 MeO groups into the styryl radical in the *o*- and *p*-positions produces a very marked increase in the auxochromic character of the radical. All auxochrome-like atomic groupings such as this 2,4-$(MeO)_2C_6H_3CH:CH$, which, thanks to the true auxochrome present in them, show increased auxochromic character, K. designates as "combined auxochromes." To characterize the colors of his compds. more exactly the powdered substances, spread on white paper, were matched against the Ostwald color scales and designated accordingly; thus, 4'-dimethylamino-4-nitrostilbene is 25*pe* and *p*-$O_2NC_6H_4NMe_2$ 00*ma*; *i. e.*, the introduction of the styryl group shifts the color very appreciably. The ability of the styryl group to play a part in the production of a combined auxochrome depends on the direct union of its CH:CH chain to its C_6H_5 nucleus; the introduction between the two of a foreign group, such as CO in B, may produce a great weakening of the auxochromic effect. B has only the color tone 00*ka*, while C is 18*pa*; similarly 4'-methoxy-4-nitrostilbene is 06*pa* and A 97*ea*. That the whole 2,4-$(MeO)_2C_6H_3CH:CH$ complex is to be considered as a *new auxochromic unit* can be shown by the aid of the partition law of auxochromes, according to which 2 MeO groups attached to the same C_6H_5 ring of a chromogen deepen the color most when in the *p*-position to each other. A comparison of C (18*pa*), D (03*pa*) and E (00*pa*) shows that the order of the relative depths of color is directly the reverse of that of the dimethoxynitrobenzenes, where the 2,5-compd. is yellow, the 3,4-compd. light yellow and the 2,4-compd. white; in the case of the dimethoxynitrostilbenes, of the 3 combined auxochromes the one having the MeO groups only in the *o*- and *p*- and not in the *m*-position to the CH:CH union is the strongest; if a combined auxochrome is considered as a single auxochromic unit the partition law of auxochromes does not apply to these compds., for the chromogen is $PhNO_2$ and to this is attached only a single auxochrome. Just like ordinary auxochromes, so also combined auxochromes favor fluorescence. 4'-Dimethylamino-4-nitrostilbene shows intense fluorescence in many solvents. 2'-Methoxy-4-nitrostilbene shows very faint yellowish green fluorescence in C_6H_6, the *p*-isomer considerably more, the 3 di-MeO compds. strong greenish yellow, the NMe_2 deriv. intense orange; in Et_2O the fluorescence is faint greenish yellow, stronger greenish yellow, strong yellow and very strong orange-red, resp. With the 3 di-MeO compds., although the fluorescence is in general similar, there are certain differences in tone and in intensity, E showing a distinctly more greenish tinge than C and the intensity increasing in the order E, D, C, a further indication that the partition law of auxochromes does not hold for these compds. In the solid state behind a blue filter C shows bright red fluorescence, E a distinctly weaker yellow fluorescence and D a very weak brownish yellow fluorescence. In its orange-yellow form with bright orange fluorescence, as obtained from ligroin, C resembles its isomers much more closely. The absorption spectrum of C in alc. shows a pronounced band with a max. at 2500 and a weaker flat band at about 3700; D has a similar spectrum but the band due to the NO_2 group is shifted to the ultra-violet (max. at 2610) and the 2nd band is less flat and at about 3500; in E the first band is still further shifted to the ultra-violet, is greatly widened and seems to run into the 2nd band. C. A. R.

Action of magnesium phenyl halides on diphenylchloroacetyl chloride. Constitution of triphenylvinyl alcohol. ALEX. MCKENZIE AND JOHN S. W. BOYLE. Univ. St. Andrews. *J. Chem. Soc.* 119, 1131–40(1921).—Forty g. $Ph_2ClCCOCl$ in 100 cc. Et_2O were gradually added within an interval of 35 min. to the Grignard reagent from 144 g. PhBr, 400 cc. Et_2O and 48 g. Mg. Upon working up as usual, 29 g. crude

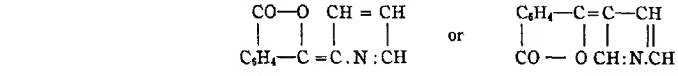
$Ph_2C:CPhOH$, and 13.3 g. Ph_2 were obtained. If the Grignard reagent is added to the chloride, Ph_2 is formed but no alc. The main product of the reaction is a hard, brown amorphous mass, from which no definite compd. could be isolated. PhMgI behaved in a similar way. The action of 3 mols. PhMgBr upon 24 g. of the alc. gave 3 g. Ph_2CHC-Ph_2OH, and much unchanged alc. 6 mols. gave a much larger quantity of the new alc. A review of the evidence on the constitution of "triphenylvinyl alcohol" is strongly in favor of the representation as $Ph_2CHCPhO$ but further proof is needed that the objections raised by Biltz (*Ann.* **296**, 242) are invalid. C. J. WEST

Esterification of naphthols in the presence of catalysts. M. ALOE. *Rend. accad. sci. Napoli* **27**, 75–80(1921).—By the reaction of Ac_2O and α- or β-$C_{10}H_7OH$ at only slightly elevated temps., α- and β-$C_{10}H_7OAc$ may be obtained, but the reactions are notably catalyzed by $FeCl_3$, P_2O_5, FeI_3, etc. (Cf. Bakunin and Giordani, *C. A.* **14**, 3653.) Using 1.44 g. of α-$C_{10}H_7OH$ and 2 cc. of Ac_2O at 31.8°, a yield of 17.6% of ester was obtained in 16.5 min. in the presence of P_2O_5, while the yield was 0 without it. At 45.9°, the yield of ester in 3.5 min. was 40.8% with $FeCl_3$, yield without it 0. With β-$C_{10}H_7OH$ and no catalyst, the yield of ester was 16% in 6 min., with P_2O_5 32.8%; with $FeCl_3$ in 35 sec., 36%; without it 15%. Phenylcinnamic anhydride and α-$C_{10}H_7OH$ were heated to boiling in $CHCl_3$ with a reflux for 10 min., the $CHCl_3$ evapd. and the residue treated with dil. Na_2CO_3, so as not to decomp. the anhydride, permitting isolation of the acid by acidifying and extg. with Et_2O, and allowing the reaction to be followed quant. The product was *α-naphthyl phenylcinnamate*, m. 119°, sol. in Et_2O, very sol. in H_2O, C_6H_6, C_7H_8, slightly sol. in petroleum ether; the yield without catalyst was 0, with $FeCl_3$ 15%. *β-Naphthyl phenylcinnamate* is less sol. than the preceding, and forms white crystals from EtOH or petr. ether, softens 115°, m.130–45°, yield without catalyst 7.1%, with $FeCl_3$ 99%. Similarly Bz_2O and α-$C_{10}H_7OH$ gave α-$C_{10}H_7OBz$, large tablets or prisms from Et_2O-EtOH, m. 56°, easily sol. in Et_2O (cf. Malkopar, *Jahresber.* **1869**, p. 489). The yield after 10 min. heating in boiling $CHCl_3$ without catalyst was 14.6%; with $FeCl_3$ 43%; in 30 min. without catalyst at 100° (no $CHCl_3$ used) 26.6%, with $FeCl_3$ 39.6%, with H_2SO_4 48.9%, with P_2O_5 33.4%. *β-Naphthyl benzoate*, slender needles from EtOH, slightly sol. in Et_2O, m. 107°. Yield without catalyst in 10 min. 14.9%, with $FeCl_3$ 43.6%. I, Cl, HCl and HBr also catalyzed the reactions. M. R. SCHMIDT

γ-Hydroxy aldehydes. III. γ-Phenyl-γ-hydroxybutyraldehyde. BURKHARDT HELFERICH AND OSKAR LECHER. *Ber.* **54B**, 930–5(1921); cf. *C. A.* **14**, 1833.—$BzCH_2$-$CH_2CH:CH_2$, from 40 g. allylbenzoylacetic ester and 32 g. KOH in 2400 cc. H_2O and 240 cc. alc., b_{14} 155–8°; *oxime*, crystals from 30% alc., m. 53–4°; *semicarbazone*, crystals from 50% MeOH, m. 156–7°. The ketone (10 g.) in 85 cc. boiling alc. treated as rapidly as possible with 5.8 g. Na in small pieces and, when all the Na has dissolved, with 2 vols. H_2O, extd. with Et_2O, shaken with $NaHSO_3$ to remove unchanged ketone and dried with K_2CO_3, gives *phenyl-γ-butenylcarbinol* (*ε-phenyl-ε-hydroxy-α-pentene*), viscous oil of peculiar aromatic odor (resembling that of ethereal oils) and of burning, bitter resinous taste, b_{10} 133–5°, b_{11} 144–4.5°, n_D^{18} 1.5220, d_4^{18} 0.980, easily volatile with steam; 1 g. in 10 g. C_6H_6 under a reflux, protected from atm. moisture, treated on the H_2O bath with 0.5 g. Na, then, after removal of the excess of Na, with 0.95 g. $C_6H_4(CO)_2O$, heated a short time longer, cooled with ice, decompd. with H_2O, drawn off from the C_6H_6, freed from the last traces of the latter by several extns. with Et_2O, covered with Et_2O, treated with ice, acidified with dil. H_2SO_4, extd. with Et_2O and dried with Na_2SO_4, gives 1.6 g. of the *hydrogen phthalate*, m. 89–90°, gradually decomps. on standing. When 10 g. of the carbinol in 18 cc. AcOH in ice is treated with 2–4% O_3 until the double bond cannot any longer be detected with Br in AcOH and the resulting ozonide or peroxide is reduced in Et_2O with Zn dust and the product is fractionated *in vacuo*, there

are obtained HCHO and 5 g. *γ-phenyl-γ-hydroxybutyraldehyde* (*2-phenyl-5-hydroxytetrahydrofuran*), b_4 137–8°, n_D^{18} 1.5410, d_4^{18} 1.126, mol. wt. in freezing AcOH 164–7, is a very viscous substance with very faint odor, immediately resinified by concd. H_2SO_4, gradually decolorizes fuchsin-SO_2, reduces boiling Fehling soln. and NH_3-$AgNO_3$ at room temp., volatile with steam, does not react when shaken with concd. NH_4OH, gradually changes on standing at room temp. with evolution of a faint but distinct cinnamon odor, becoming turbid and slowly yellow; 8 g. in 60 cc. dry MeOH containing 1% HCl allowed to stand 35 hrs., then treated with 1 g. solid K_2CO_3, evapd. *in vacuo* at 20–30°, taken up in 100 cc. Et_2O and filtered yields 4.5 g. of the *methyl hemiacetal*, b_{25} 134–6°, n_D^{18} 1.5120, d_4^{18} 1.058, is a mobile liquid of aromatic odor, does not reduce Fehling soln. on short boiling but is hydrolyzed by heating with mineral acids, a sample showing slight reduction with Fehling soln. after heating 4 hrs. on the H_2O bath with 3 *N* HCl and carefully neutralizing with $NaHCO_3$. From 1.5 g. of the aldehyde and 5 g. of 10% NaOH shaken with 2 g. $KMnO_4$ in 80 cc. H_2O until the $KMnO_4$ is decolorized and allowed to stand some hrs. is obtained $BzCH_2CH_2CO_2H$. *γ-Phenyl-γ-ketobutyraldehyde* (4.5 g. from 10 g. $BzCH_2CH_2CH:CH_2$ with O_3), $b_{2.8}$ 131°, n_D^{18} 1.5412, d_4^{18} 1.134, gradually decolorizes fuchsin-SO_2, slowly reduces Fehling soln. even at room temp. and alk. NH_3-$AgNO_3$ almost instantly at room temp., forms when moistened with 10 *N* NaOH a yellow ppt. soon becoming yellowish and with concd. NH_4OH a viscous amorphous mass, converted by a slow current of dust-free air in 2 days into $BzCH_2CH_2CO_2H$, while 1 g. in 5 g. of 50% AcOH with 0.8 g. $PhNHNH_2$ in 5 g. 50% AcOH and 5 g. glacial AcOH yields 1.9 g. crude or 0.6 g. pure *1,6-diphenyl-1,4-dihydropyridazine*, PhN.N:CH.CH_2.CH:CPh, prisms from Me_2CO-H_2O (4:1), m. 244–5°, practically insol. in acids and alkalies, yields no HCl salt with dry HCl in Et_2O. CHAS. A. ROUILLER

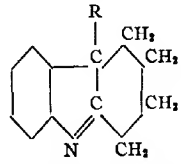
Products of the action of phthalic anhydride upon pyrroles and indoles. G. PLANCHER. *Giorn. chim. ind. applicata* **2**, 458–9(1920).—Boiling $PhNH_2$ for a long time with pyrrolic and indolic derivs. of $C_6H_4(CO)_2O$ gives a means of distinguishing between the N and the C derivs. The first are broken up and the second are unaltered. Thus C_6H_4.CH:CMe.NCO$C_6H_4CO_2H$ gives methylketol and $C_6H_4(CO)_2NPh$, while the pyrrolenephthalide is unaltered. This confirms the conclusions of Ciamician, who attributed to pyrrolenephthalide (obtained by Ciamician and Dennstedt by the action of pyrrole upon $C_6H_4(CO)_2O$) either of the following formulas:



ROBERT S. POSMONTIER

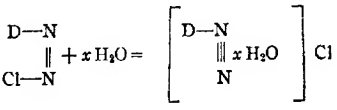
Action of malonic ester upon *p*-benzoylmethyltrimethylindolene. G. PLANCHER AND F. CARAVITA. *Giorn. chim. ind. applicata* **2**, 458(1920).—The authors treated *p*-C_6H_4.NH.CHMe.CMe_2, with $CH_2(CO_2Et)_2$, and obtained, instead of diketomethylindolene (as did Bamberger and Sternitzki with dihydro-α-methylindole; *Ber.* **26**, 1291), the Ac deriv. of the original base, C_6H_4.NAc.CHMe.CMe_2, with elimination of alc., C_6H_4 and CO_2. They showed that their method of indirect acetylization may be made useful with bases that are non-resistant in an acid medium. ROBERT S. POSMONTIER

Synthesis of hydrogenated carbazoles from phenylhydrazones of cyclic ketones. G. PLANCHER, G. TESTONI AND F. OLIVARI. *Giorn. chim. ind. applicata* **2**, 458 (1920).—The authors find, contrary to W. Borsche, that on condensing phenylhydrazones of the cyclohexanone homologs, either with $ZnCl_2$, alc. H_2SO_4 or aq. H_2SO_4, car-

bazolenines are formed, when either a CH_2, a CHMe or two CHMe groups are in proximity to the ketonic group of the original ketone. These carbazolenines have the structure  and are bases analogous to the indolenines and isomeric with the tetrahydrocarbazoles. ROBERT S. POSMONTIER

Reactions of formamidines. IX. Synthesis of 5-phenyl-4-pyrazolecarboxylic acid. F. B. DAINS AND W. S. LONG. *J. Am. Chem. Soc.* **43**, 1200–2(1921); cf. *C. A.* **12**, 904.—PhNHCOC(:CPhOH)CH:NPh (7 g.), 11.09 g. $N_2H_4.H_2SO_4$, 1 equiv. dry Na_2CO_3 and 75 cc. EtOH boiled 5 hrs. under a reflux give *5-phenyl-4-pyrazolecarboxanilide*, crystals with 1 mol. solvent from MeOH or EtOH, m. 182°; *hydrochloride*, prepd. in dry C_6H_6, is unstable; free *acid*, from the anilide boiled several hrs. with concd. HCl, fine silky needles from H_2O, m. 260°; *ethyl ester*, from Et *o*-phenetidylaminomethylenebenzoylacetate and N_2H_4, needles from dil. alc., m. 85–6°, does not form a HCl salt, Ac or Bz deriv. and does not add MeI. At 260–70° the acid loses CO_2 and yields 5-phenylpyrazole, m. 78°. Neither the acid nor its ester reacts with $PhNH_2$, even after several hrs. at 200°. *p-Anisidide*, from N_2H_4 and *p*-anisidylaminomethylenebenzoylacet-*p*-anisidide, long needles from dil. alc., m. 161°. *o-Anisidide*, m. 127°, hydrolyzed to the acid only by boiling with concd. HBr. C. A. ROUILLER

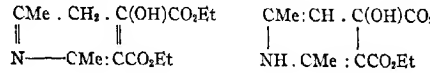
Diazo derivatives of 4'-amino-1-phenyl-5-methylbenzothiazole (dehydrothio-*p*-toluidine). GILBERT T. MORGAN AND DOROTHY WEBSTER. Univ. Birmingham. *J. Chem. Soc.* **119**, 1070–7(1921).—4'-Amino-1-phenyl-5-methylbenzothiazole (A) (Green, *J. Chem. Soc.* **55**, 227) on being diazotized yields 2 isomeric compds., an insol. diazo-chloride and a sol. product, pptd. by Et_2O, which have the properties of the *syn*- and *anti*-diazocyanides derived from simpler aromatic amines. The *syn*-deriv. is readily sol. in H_2O, couples with alk. β-$C_{10}H_7OH$, and reacts readily with Cu bronze, while the *anti*-deriv. is insol. in H_2O, does not couple with β-$C_{10}H_7OH$ and reacts slowly with Cu bronze. The soly. of the *syn*-deriv. in H_2O suggests that it passes readily into the diazonium condition:



salt, 15 g. A were converted into the HCl with alc. HCl, the dry salt suspended in about 50 cc. abs. alc. and treated at 0° with 9 g. $EtNO_2$ in 50 cc. alc. The sparingly sol. *anti-1-phenyl-5-methylbenzothiazole-4'-diazochloride*, $C_{14}H_{10}N_3ClS$, brownish yellow, amorphous powder, m. 270°, while the sol. *syn*-deriv. m. 139°. With β-$C_{10}H_7OH$ this gave *1-phenyl-5-methylbenzothiazole-4'-azo-β-naphthol*, $C_{24}H_{17}ON_3S$, crimson needles, m. 214°; the H_2SO_4 soln. is violet. The aq. soln., treated in the cold with Cu bronze, gave *4'-chloro-1-phenyl-5-methylbenzothiazole*, $C_{14}H_{10}NClS$, pale yellow, granular nodules, m. 160°. The *anti*-deriv. gave the same Cl deriv. after 1 week. The *potassium salts* were prepd. but were not obtained pure. The action of NaN_3 upon the *syn*-diazochloride gave *4'-triazo-1-phenyl-5-methylbenzothiazole*, $C_{14}H_{10}N_6S$, light brown powder, m. 121°. With the *anti*-deriv., NaN_3 gives A. Na_2SO_3 in NaOH gave the *syn-diazosulfonate*, orange-brown amorphous ppt., m. 202°. The *anti-diazosulfonate* forms a yellow

amorphous product, m. 309°. *syn-Diazocyanide*, $C_{15}H_{10}N_4S$, brick-red, very sol. in H_2O and decomps. 131°. The *anti-derivative* is deep orange, may be crystd. from moist Me_2CO and m. 175°. Additions of Cu to the *syn*-deriv. gave *4'-cyano-1-phenyl-5-methylbenzothiazole*, $C_{15}H_{10}N_2S$, yellow, m. 145°. The following *syn*-salts were obtained: *Nitrate*, $C_{14}H_{10}O_3N_4S$, yellowish brown, explodes at 145°. *Acid chromate*, $C_{14}H_{11}O_4N_3SCr$, yellow, detonates 120°. *Nitroprusside*, $C_{33}H_{20}ON_{12}S_2Fe$, bright yellow, explodes 140°. *Ferricyanide*, $C_{48}H_{30}N_{18}S_3Fe$, greenish yellow powder, m. 158°. *Acid carbonate*, $C_{15}H_{11}O_3N_3S$, reddish brown amorphous powder, m. 128° with slight detonation. *Chlorate*, $C_{14}H_{10}O_3N_3ClS$, brilliant yellow amorphous powder, exploding violently at 110°. *Orthoborate*, $C_{42}H_{30}O_3N_6S_3B$, bright brown powder, m. 154° (decompn.). C. J. West

Synthesis of some carboxylic acids and ketocarboxylic acids of pyridine. Otto Mumm and Otto Böhme. Univ. Kiel. *Ber.* **54B**, 726–37(1921).—In order to test whether the reaction whereby di-Et 2,6-dimethyl-3,4-cinchomeronate is obtained from $AcCH:C(OH)CO_2Et$ (A) and $H_2NCMe:CHCO_2Et$ (B) (*C. A.* **12**, 1878) is of general applicability for the prepn. of C_5H_5N derivs., M. and B. made a series of expts. in which they varied one of the above components while keeping the other const., and they have found that, like the Hantzsch-Knövenagel synthesis, the method yields dicarboxylic and ketocarboxylic acids of C_5H_5N, and, in fact, such as cannot be obtained by the H.-K. method, *viz.* those with a CO_2H group in position 4, and contrary to the H.-K. method, the new one gives directly the C_5H_5N derivs. without the necessity of having to pass through the dihydro compds. The mechanism of the reaction, in its first stages, is probably analogous to that of the H.-K. synthesis, *i. e.*, there is probably first formed an addition product of the type $MeCOCH_2C(OH)(CO_2Et)C(CO_2Et):CMeNH_2$ or $MeC(OH):CHC(OH)(CO_2Et)C(CO_2Et):CMeNH_2$ which by loss of 1 mol. of H_2O forms a *p*-hydroxydihydro ester, (I) or (II); this is unstable and at once loses a 2nd mol. of H_2O to form the non-hydrogenated ester. Of the 2 formulas for the intermediate product, I is given the preference.



I

II

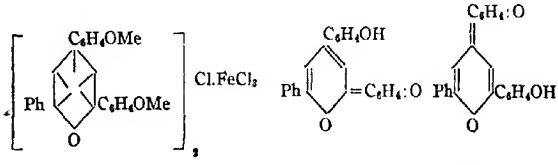
$EtCOCH:C(OH)CO_2Et$ (C), $b_{0.6-1.0}$ 80–4° (Diels, Sielisch and Müller, *Ber.* **39**, 1333 (1906)), is obtained in somewhat greater yield (51 instead of 40–4%) if, to decomp. the Na salt first formed, the reaction mixt. is dild. with an equal vol. of Et_2O, treated dropwise with the calcd. amt. of H_2SO_4 of such a concn. that the H_2O is just taken up by the Na_2SO_4 as the decahydrate, filtered from the latter, washed once with a very little H_2O, dried over Na_2SO_4 and fractionated. From 25 g. C vigorously shaken in the cold with 19 g. B, allowed to stand overnight in the ice chest, warmed a short time on the H_2O bath, taken up in Et_2O, washed a few times with H_2O containing a few drops of Na_2CO_3 at 0° and carefully dried is obtained 32 g. *diethyl 2-methyl-6-ethylcinchomeronate*, thick yellowish oil, $b_{0.4-0.8}$ 140–5°; it is also obtained in 90% yield by carrying out the condensation in Et_2O, adding Na_2SO_4 to combine with the H_2O and allowing to stand 24 hrs. in the ice chest and 3 days at room temp. *Picrate*, fine yellow needles from alc., m. 90°. Free *acid*, from 13.3 g. of the ester boiled 3 hrs. with 50 cc. of 4 *N* NaOH and then exactly neutralized with 4 *N* HCl, crystals from H_2O, m. 258–9°. When 11 g. $BzCH:C(OH)CO_2Et$ in 6 g. alc. and 6.5 g. B in 2 g. alc., each cooled to incipient crystn., are mixed, the mixt. solidifies, sometimes in a few sec. but usually only after standing overnight in the ice chest, to a white mass consisting of a mixt. of the expected ester and the intermediate *addition product*, $C_{18}H_{23}O_6N$, sepd. by crystn. from AcOEt in

which the latter is much less sol., but during the crystn. the solns. must never be kept long at a high temp. as the intermediate product is more or less completely converted into the stable end product. It forms short stout prismatic needles, m. 148° (foaming), the resolidified melt now containing pure *diethyl 2-methyl-6-phenylcinchomeronate*, which also seps. on partial evapn. of the AcOEt mother liquors in long silky needles, m. 73°; it is best prepd. by boiling the original reaction mixt. with a little alc. to decomp. the intermediate product. *Picrate*, m. 83°. Free *acid* (yield, 92%), crystals from alc., m. 217° (foaming). *Diethyl 2-methyl-6-propylcinchomeronate* (89% from PrCOCH:C(OH)CO_2Et and B), yellow oil, b_{12} 174–6°; *picrate*, crystals from alc., m. 115–6°; free *acid* (yield, 89%), stout tables with 1 H_2O, m. 212° (foaming). *iso*-PrCOCH:C(OH)-CO_2Et and B mixed at room temp. and strongly cooled yield the *addition product*, $C_{15}H_{25}O_6N$, crystals from AcOEt, m. 87°, which on long standing with or without solvent at room temp., quickly and easily at a higher temp., passes over into *diethyl 2-methyl-6-isopropylcinchomeronate* (best prepd. by heating the original reaction mixt. a short time on the H_2O bath), light yellow oil, b_{11} 178° (yield, 90%); *picrate*, m. 116°; free *acid*, seps. in almost quadratic tables with 2 H_2O on strong cooling, in anhydrous form when crystd. slowly, m. 210° (foaming). $Me_3CCOCH:C(OH)CO_2Et$ and B yield the *addition product*, $C_{16}H_{27}O_6N$, prismatic columns from AcOEt, m. 94°, passing over at room temp., more quickly on heating, into *diethyl 2-methyl-6-tert-butylcinchomeronate* (best prepd. by heating the reaction mixt. 10 min. on the H_2O bath; yield, 64%), b_{12} 172°; *picrate*, fine yellow needles from alc., m. 127°; free *acid* (yield, almost quant.), crystals with 2 H_2O which it loses at 137°, melting, resolidifying and m. again 208°. From equimol. amts. of AcCH:$CMeNH_2$ and A shaken in the cold until a clear soln. results, allowed to stand 20 hrs. in the ice chest., heated a short time on the H_2O bath, taken up with Et_2O, washed several times with very dil. cold NaOH and dried with Na_2SO_4 is obtained 65% of *ethyl 2,6-dimethyl-3-acetylpyridine-4-carboxylate*, yellow oil, b_{12} 154–5°, crystals from petr. ether, m. 30–1°; *picrate*, m. 160°; free *acid*, from the ester boiled 3 hrs. with 3 mols. of 11 *N* HCl, evapd. to dryness and crystd. from alc., m. 206–7°. *Ethyl 2,6-dimethyl-3-benzoylpyridine-4-carboxylate hydrochloride*, from 1 mol. each of A and BzCH:$CMeNH_2$ treated with 1 mol. of 7*N* HCl in abs. alc., needles, m. 188–9°, converted by an excess of cold 2 *N* NaOH into the free *ester*, extraordinarily viscous oil (60% yield), b_{12} 220°, granular crystals from alc., m. 66°; boiled 10 hrs. with 10 mols. 2 *N* HCl it gives the free *acid*, crystals from H_2O, m. 255–8°.

CHAS. A. ROUILLER

Pyrylium compounds. X. The violones. W. DILTHEY AND B. BURGER. Univ. Erlangen. *Ber.* **54B**, 825–30(1921); cf. *C. A.* **15**, 1239.—*p*-$MeOC_6H_4CH$:CHCOPh (8 g.) and 5 g. *p*-$MeOC_6H_4COMe$ in 40 cc. Ac_2O treated with crystd. $FeCl_3$ until a thick cryst. magma results yields *2,4-di-(p-methoxyphenyl)-6-phenylpyrylium chloride-ferric chloride* (I), orange-red crystals from Me_2CO-Et_2O, m. 225°, shows bright yellow fluorescence in AcOH; pptd. from H_2O with soda, extd. with C_6H_6 and recrystd. from gasoline it gives the corresponding pseudo base, *α,γ-di-p-anisyl-δ-benzoyl-α-hydroxy-α,γ-butadiene*, in almost pure white cryst. warts, m. 97–9°, which, however, on filtering, even when the air is excluded, always turn yellow; this change also occurs when the gasoline mother liquor is allowed to stand some days, and the colorless form could not be isolated; the solns. in AcOH and in concd. H_2SO_4 show strong green-yellow fluorescence while the undissolved particles are brick-red. *Picrate*, orange-red crystals from AcOH, m. 250–1°. Treated in alc. with concd. HCl, the pseudo base gives an *acid chloride*, $C_{28}H_{21}O_3Cl.HCl$, velvety orange crystals, m. 106–7° on rapid heating, resolidifies and m. again 194°; attempts to split off the HCl by repeatedly crystg. from Me_2CO-Et_2O or by treating in C_6H_6 suspension with dry air 10 hrs. in the cold and 24 hrs. at 50–60° led only to the loss of 0.5 mol. HCl and no change in the m. p. *Chloroplatinate*, orange cryst. powder

from AcOH, m. 235–6°. When the pseudo base is heated 6 hrs. in a sealed tube with concd. HCl at 160–80° it gives *2,4-di-p-hydroxyphenyl-6-phenylpyrylium chloride* in two forms (dark red crystals and (in smaller amt.) lighter prisms), which do not m. 350°, show the same yellow-green fluorescence in H_2O and alc., sol. in alc. with orange color changing with dil. alkalies to violet-red with pptn. of violone, but an excess of alkali, even $NaHCO_3$, redissolves the ppt. with a red-yellow color similar to that of the acid solns. *2-p-Hydroxy-4-violone* (II) or (III), from the above chloride in very dil. hot



I II III

soda just acidified with AcOH, stout crystals with greenish luster from C_5H_5N, m. 317°, sol. in hot alkalies and soda with brown color (yellow in very dil. solns.) and in acids with yellow color; treated in C_5H_5N with H_2O it yields the amorphous *pseudo base*, obtained as the *dibenzoate*, $BzOC_6H_4C(OH):CHC(C_6H_4OBz):CHCOPh$, by allowing the violone in 150–200 cc. C_5H_5N to stand 1 day with 1 g. BzCl or from the violone in dil. soda shaken in the cold with BzCl; this m. 147°, dissolves in org. solvents without color or fluorescence but in AcOH with an extraordinarily strong yellow-green fluorescence, also produced on addition of a little HCl to the alc. soln., but as the result of the splitting off of the Bz groups this fluorescence soon disappears and is replaced by the orange-yellow color of the violone; alkalies and soda, the latter on heating, also easily split off the Bz groups. *Dibenzoate picrate*, red-yellow prisms from alc. or Me_2CO, m. 215°. Of the formulas II and III for the violone, III is given the preference because the color of the compd. (red-violet) is intermediate between that of the simplest 2-violone (violet) and the simplest 4-violone (distinctly violet-red) and if the new compd. were a 2-violone it would be expected to be bluer than the simplest 2-violone.

CHAS. A. ROUILLER

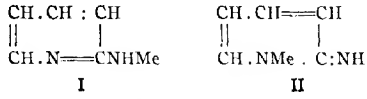
The chromones and flavones. S. RUHEMANN. Univ. Berlin. *Ber.* **54B**, 912–24 (1921).—*Ethyl β-3-methyl-5-methoxyphenoxycinnamate*, from 8 g. 3,5-Me(MeO)C_6H_3OH in xylene boiled with 1.2 g. Na until the Na dissolves, then boiled about 2 hrs. with 8.7 g. $PhC:CCO_2Et$, cooled, acidified with dil. H_2SO_4, extd. with Et_2O, freed from the excess of phenol with KOH, washed with H_2O and dried with $CaCl_2$, yellow, exceedingly viscous oil, hydrolyzed by boiling 1 hr. with alc. KOH to the *acid*, prisms from dil. alc., sinters 122°, m. completely 140° (gas evolution); treated in C_6H_6 suspension with the calcd. amt. of PCl_5 and, when the reaction is complete, with $AlCl_3$, then decompd. with ice and extd. with Et_2O, it yields *5(7)-methyl-7(5)-methoxyflavone*, b_{14} about 255°, needles from dil. alc., m. 99–100°, sol. in concd. H_2SO_4 with yellowish color and blue fluorescence. For the synthesis of chlorochromones and chloroflavones the chlorophenols are converted into the Na salts with the calcd. amt. of Na in alc., freed from the alc. *in vacuo* (finally at 150°) and boiled 2 hrs. in xylene with $PhC:CHCO_2Et$ or chlorofumaric ester. The reaction, however, proceeds more rapidly and the yields are almost quant. if an excess of the chlorophenol (about once as much again as that used in making the Na salt) is used as diluent and the temp. is raised for a few min. almost to the boiling point of the chlorophenol; the excess of the latter can then be removed by distn. *in vacuo* or by treatment of the Et_2O ext. of the acidified reaction mixt. with dil. KOH. *Diethyl o-chlorophenoxyfumarate* (22–3 g. from 20.8 g. chlorofumaric ester), b_{14} 203–4°; free *acid*, yellow

octahedrons from H_2O, m. 202–3° (gas evolution), converted after standing 1 day in concd. H_2SO_4 into *8-chlorochromone-2-carboxylic acid*, needles from dil. alc., m. about 260° (gas evolution); heated until the evolution of CO_2 ceases and distd. *in vacuo*, it yields *8-chlorochromone*, spears from EtOH-H_2O, m. 114–5°, sol. in cold concd. H_2SO_4 with yellow color but no fluorescence. *Diethyl p-chlorophenoxyfumarate* (21–2 g. from 13 g. *p*-ClC_6H_4OH and 2.3 g. Na in alc. and, after removal of the alc., 15 g. more ClC_6H_4OH and 20.8 g. chlorofumaric ester), b_{12} 199–200°; *acid*, yellow rhombic crystals from H_2O, m. 211–2° (gas evolution), converted after 1 day in concd. H_2SO_4 into *6-chlorochromone-2-carboxylic acid*, needles from alc., m. 261–2° with loss of CO_2 and formation of *6-chlorochromone*, leaflets from alc., m. 139–40°, sol. in cold concd. H_2SO_4 with faint blue fluorescence. *Ethyl β-o-chlorophenoxycinnamate* (11–2 g. from 7 g. *o*-ClC_6H_4OH and 1.2 g. Na, heated, after removal of the alc., a few min. with about 10 g. more ClC_6H_4OH and 8.7 g. PhC : $CHCO_2Et$), thick oil, b_{15} 218–20°; *acid*, prisms from dil. alc., sinters about 130°, gradually decomps. and m. completely 160°; distd. *in vacuo*, it loses CO_2 and forms *α-o-chlorophenoxystyrene*, yellow oil with an odor like that of *o*-ClC_6H_4OH, b_{14} 178°. *8-Chloroflavone*, needles from alc., m. 169–70°, sol. in concd. H_2SO_4 with faint yellow color but no fluorescence. *Ethyl β-p-chlorophenoxycinnamate* (5 g. from 7 g. *p*-ClC_6H_4OH (converted into the Na salt) heated nearly to boiling with 8.7 g. PhC : $CHCO_2Et$ and 12–4 g. free ClC_6H_4OH), thick yellow oil, b_{12} 220–5°, stout prisms from petr. ether, m. 63–4°; *acid*, prisms from alc., softens 128°, decomps. 136°. *6-Chloroflavone*, long needles from alc., m. 183–4°, dissolves in H_2SO_4 with a yellow color which soon disappears and is replaced by a blue fluorescence. *Ethyl β-3-methyl-4-chlorophenoxycinnamate* (9 g. from 7.3 g. 3,4-$MeClC_6H_3OH$ and 8.7 g. PhC : $CHCO_2Et$), thick, light yellow oil, b_{14} 231–2°, prisms from alc., m. 92–3°; *acid*, prisms from alc., sinters about 140°, m. 155° (gas evolution). The product formed by the successive action of PCl_5 and $AlCl_3$ on the acid seps. from alc. in prisms m. indefinitely 145–7° and probably consisting of a mixt. of the isomeric *5-* and *7-methyl-6-chloroflavones*. *Ethyl β-p-benzeneazophenoxycinnamate*, from 10 g. *p*-HOC_6H_4N:NPh treated with 1.2 g. Na in alc., freed from the alc. *in vacuo* (finally at 150°) and boiled 2 hrs. in xylene under a reflux with 8.8 g. PhC : $CHCO_2Et$, orange prisms from alc., m. 156° (yield, 2.5 g.); *acid*, yellow-red prisms from AcOH-H_2O, m. 184–5° (gas evolution), forms a difficultly sol. yellow *sodium salt*. *6-Benzeneazoflavone*, yellow prisms from alc., m. 194–5°.

CHAS. A. ROUILLER

Tautomerism of *o*-aminopyridine and its derivatives. A. E. CHICHIBABIN, R. A. KONOVALOVA AND A. A. KONOVALOVA. *Ber.* **54B**, 814–22(1921); cf. *C. A.* **9**, 1901.—While MeI acting on the Na derivs. of α-aminopyridine (A) and its homologs yields sec. (I) and tert. α-aminopyridines, it has now been found that by the direct action of MeI on A there are obtained as chief products derivs. (II) of the tautomeric or α-pyridone-imide form of A. Whether there is first formed a methiodide of A which then rearranges into II under the influence of the alkali or whether the methiodide immediately isomerizes to the HI salt of II cannot yet be detd. with certainty. While I is a stable substance which can be distd. under atm. pressure, can be kept in the air a long time and forms stable salts with mineral acids (although it is a weak base, forming no carbonate), II is much less stable, soon becoming red in the air, then dark, eagerly absorbs CO_2, is unchanged by hot concd. HCl but is easily decompd. by alkalies. The methylation of A under different conditions always leads to a mixt. of both I and II, but I is always the chief product when the Na deriv. of A is used and II when the A is methylated directly. Freshly distd. A (22 g.) in 100 cc. Et_2O is treated under a reflux with 9 g. $NaNH_2$ carefully powdered in a warm mortar, boiled 2 hrs., cooled, slowly treated with 33 g. MeI, boiled 1 hr. longer, worked up with cold H_2O, the Et_2O soln. dried with Na_2SO_4, fractionated under atm. pressure, the mixt. of bases (b. 180–201°) in Me_2CO

pptd. with picric acid and the picrates crystd. from hot H_2O; there are thus obtained the orange-yellow needles, m. 190°, of the picrate of I, which is an oil, b. 200–1°, of a peculiar odor somewhat resembling that of A. The concd. aq. and Me_2CO solns. deposit mixts. of picrates sepd. by repeated crystn. from H_2O into the above picrate and α-dimethylaminopyridine picrate, m. 182°. In a later expt. there was obtained, besides the above bases and unchanged A, a small amt. of a mixt. of bases which could not be liberated from the salt solns. by means of soda and from which was isolated the picrate, m. 201° (see below), of II. When 20 g. A and 34 g. MeI are mixed under a reflux an energetic reaction soon sets in and is complete in a few min.; on cooling the whole mixt. solidifies and on crystn. from alc. yields 36.5 g. of a *compound*, $C_6H_9N_2I$, yellowish prisms exceedingly sol. in H_2O, m. 149–50°, eagerly absorbs moisture, converted by double decompn. into a *picrate*, yellow needles, m. 201°, and a *chloroplatinate*, orange needles, m. 204°. The mother liquors from the iodide, after evapn. on the H_2O bath, treatment in H_2O with soda and extn. with Et_2O, yield a small amt. of a mixt. of unchanged A and of I. From 6 g. of the above iodide shaken with 3.5 g. freshly pptd. Ag_2O, filtered and evapd. *in vacuo* is obtained *N-methyl-α-pyridone-imide* (II),



I II

thick greenish liquid, b_{16} 108°, crysts. on cooling, also obtained by cautiously treating the iodide in H_2O with excess of alkali and extg. with warm C_6H_6, deliquesces in the air; *hydrochloride*, prisms from alc., m. 110°. With PhNCO II gives a *compound* sepg. from alc. in needles, m. 148°; with BzCl by the Schotten-Baumann method is obtained *N-methyl-α-pyridone-benzoylimide*, golden yellow granular crystals from Et_2O, m. 70°. II (3.5 g.) boiled 6 hrs. with 7 g. KOH in 20 cc. H_2O decomps. almost quant. into NH_3 and *N*-methyl-α-pyridone. From 10 g. II in 5 cc. alc. treated with 14 g. MeI is obtained a *compound*, $C_7H_{11}N_2I$, prisms from alc., m. 159–60°, yielding a *picrate*, m. 160°, 9 g. of which in 20 cc. H_2O treated with concd. KOH until an oil sepd., then extd. with C_6H_6 and dried with K_2CO_3, gave *N-methyl-α-pyridone-methylimide*, thick yellowish liquid, b_{28} 128°, quickly becomes dark green in the air, eagerly absorbs CO_2. I with MeI yields a cryst. mixt. of iodides from which the above iodide, m. 159–60°, can easily be isolated by fractional crystn. from alc. A (6.2 g.) allowed to stand 1 day with 8.4 g. $PhCH_2Cl$ in alc. and evapd. on the H_2O bath yields 6 g. of a *hydrochloride*, m. 202–3°, forming a *chloroplatinate*, red cryst. powder, m. 210°, and yielding with alkalies *N-benzyl-α-pyridone-imide*, hygroscopic crystals, m. 37–9°, deliquesces in the air, reacts much more slowly with alkalies than II, long boiling with alc. KOH being necessary to complete the decompn. into NH_3 and *N*-benzyl-α-pyridone. The mother liquors from the hydrochloride, when evapd. on the H_2O bath, taken up in H_2O, freed from neutral products with Et_2O, pptd. with soda, taken up with Et_2O and dried with BaO, yielded *α-benzylaminopyridine*, flat prisms from C_6H_6, m. 93–4°, quite stable in the air, sol. in dil. mineral acids and repptd. by soda; *chloroplatinate*, red cryst. druses, m. 175°.

CHAS. A. ROUILLER

Action of methyl iodide on α- and γ-quinoline. A. E. CHICHIBABIN. *Ber.* **54B**, 822–5(1921); cf. preceding abstr.—C. believes that a methylquinolone-imide structure analogous to that of the pyridone-imides whose discovery is reported in the preceding paper better represents the properties of the Et_2O-sol. bases obtained by Claus and his pupils by the action of MeI on α- and γ-aminoquinoline and subsequent treatment with Ag_2O than the alkylidene structure which he assigned to them (*J. prakt. Chem.* **56**, 181 (1897)). The quinolone-imide formula also gives a simple explanation of the reaction,

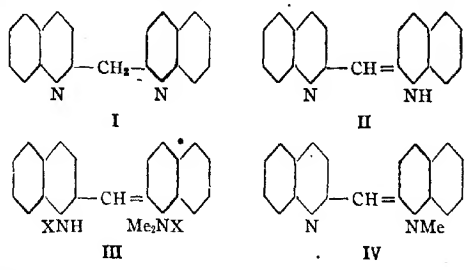
observed by Roser (*Ann.* 282, 373(1894)), between BzCl and the base from α-amino-quinoline, whereby is formed a substance to which R. assigned the structure of an "anhydro product." CHAS. A. ROUILLER

Cinchona alkaloids. XXII. Synthesis of 3-acetyl-4-methylpyridine and of β-collidine. PAUL RABE AND ERNST JANTZEN. Univ. Hamburg. *Ber.* **54B**, 924–9 (1921); cf. *C. A.* **14**, 1980.—The crude 4,3-$C_5H_3NMeCO_2H$, obtained by oxidation of lepidine with $KMnO_4$, gives with alc. and H_2SO_4 90% *ethyl 4-methylpyridine-3-carboxylate* (*ethyl homonicotinate*), strongly refractive, hygroscopic liquid, b_{12} 118°; *picrate*, felted golden yellow needles from alc., m. 137°, sol. in 270 parts alc. at room temp., in 10–11 parts boiling alc.; *chloroplatinate*, orange-yellow needles from dil. HCl, m. 183° (decompn.). When 13.6 g. of the ester and 9 g. AcOEt are dropped into 6.8 g. NaOEt in 7 cc. C_6H_6 at 80°, heated 5 hrs. longer, poured upon ice, freed from unchanged ester with Et_2O (the Et_2O ext. must be repeatedly washed with ice-cold NaOH and the washings added to the original alk. soln.), heated 3 hrs. on the H_2O bath with an equal vol. of concd. HCl, neutralized, satd. with NaCl and extd. with Et_2O, it yields (besides 4.6 g. unchanged ester in the Et_2O), 4 g. *3-acetyl-4-methylpyridine*, b_{12} 105°, smells of mouse excrement when dil.; *picrate*, broad golden yellow scales from alc. on rapid, very short needles on slower cooling, sol. in 37 parts boiling and 200 parts cold alc.; *chloroplatinate*, light ocher-colored prismatic needles from dil. HCl, m. 206–7° (decompn.); *chloroaurate*, obtained not quite pure on account of the reducing action of the ketone, egg-yellow ppt. from hot HCl; *hydrazone*, from 4.8 g. of the ketone and 4.6 cc. $N_2H_4.H_2O$ heated 12 hrs. at 115–25°, very thick, faintly yellow oil which, when heated slowly with 0.1 g. powdered KOH to 180° and kept 2 hrs. at this temp. yielded 3.6 g. β-collidine, b_{12} 76°, identical with the product obtained from cinchonine or meroquinene.

CHAS. A. ROUILLER

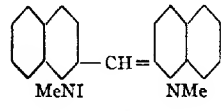
Di- and triquinolylmethanes joined through the pyridine nucleus. II. *sym*-Diquinolyl-2-methane and the synthesis of pseudoisocyanine and of quinoline red. GÜNTHER SCHEIBE AND ROSSNER. E. Düsseldorfer Akad. f. Medizin. *Ber.* **54B**, 786–95(1921); cf. *C. A.* **15**, 1308.—If 2-chloroquinoline is heated with 1.5–2.0 mols. quinaldine, best in a sealed tube, 1 hr. at 180–210°, there appears a brown-red color which slowly increases. After cooling, the contents of the tube are extd. with alc. KOH and the unchanged starting material is removed with steam, leaving a red tar containing, besides *diquinolyl-2-methane* (A), varying amts. of triquinolyl-2-methane (B), characterized by its permanent red color in excess of acids and by its absorption band. The sepn. can be effected in 2 ways, the 1st being the more satisfactory when the amt. of B is only small. (1) The tar in 20–30 parts hot alc. is treated with excess of hot alc. picric acid, the dipicrate of A sepg. at once in yellow crystals which are filtered off before the soln. is completely cold, dissolved in hot H_2O and made alk. and the free A is extd. with Et_2O. (2) The tar in C_6H_6 is shaken with small portions of *N* HCl until the C_6H_6 is almost free of solute, the exts. are made alk. and those parts of the pptd. base which are light yellow-red and dissolve almost without color in excess of acid are collected separately and extd. with Et_2O. The dried Et_2O solns. obtained in either case give on evapn. faintly yellow-red stout prisms, begin to redden 98°, m. 102–3°, sol. in all org. solvents without color in the cold, but on warming the solns. become intensely yellow-red and show 2 absorption bands in the green; if the alc. soln. is treated with a little acid the color becomes wine-red, while further addition of acid produces finally complete decolorization; alkalies regenerate the original substance. The Et_2O mother liquors from the above crystals are yellow-red and show the same absorption bands as the solns. of the white base; on further evapn. there is obtained, in varying yield, long fiery red needles becoming somewhat lighter at 95° and m. 103° (mixed with the white substance, they m. 102–3°); on standing, the alc. soln. pales out somewhat; addition of alkali ppts. oil droplets

solidifying to silky needles identical with the white compd.; with acids, the red behaves exactly like the white compd. The conversion of the white into the red compd. is partially effected by warming the solns. or fusing the solid, an equil. being established. The white form of A is believed to have the structure I and the red form the desmotropic structure II, the colorless salts, with 2 mols. acid, being derived from I, and the colored monoacid salts from II. *Dipicrate*, yellow crystals, m. 210° (decompn.); *monopicrate*, from exactly equimol. amts. of A and picric acid in hot MeOH, felted red needles with green surface luster, containing 1 MeOH, decomps. 239°. (B forms an analogous *picrate*, almost black-violet needles, decomps. 239°.) A heated 4 hrs. in alc. at 100° with excess of MeI adds 2 mols. MeI, forming a *compound*, orange-red prisms from H_2O, rubbing to an ocher-yellow powder, decomps. about 205°, gives with alkalies HI+MeI; it is assigned the structure III. Treated in H_2O with alkali and extd. with Et_2O, III yields *N-methyl-2-quinolylenequinaldine* (IV), best prepd. from exactly equimol. amts. of A and Me_2SO_4 in a little alc. heated on the H_2O bath until the solvent is expelled and then heated 1 hr. longer, extd. with a little alc. and treated dropwise with alkali; it forms red, elongated, 6-sided tables with metallic reflex, m. 156° (yield, 0.52 g. from 0.54 g. A). In IV there is no labile H atom corresponding to that in II, its place being taken by Me, and IV cannot be converted by alkalies into a form corresponding to I and with acids forms only the colored monoacid salts; thus, picric acid, even in excess, gives only the *monopicrate*, dark red needles with metallic luster from alc. containing picric acid, decomps. 184°. IV in AcOH, in which it dissolves with the intense color and the two absorption bands of isocyanine, when titrated with Br until the two bands disappear and are replaced by a weak diffuse band, the color changing from an intense wine-red to a faint bluish color, absorbs 2 atoms Br; if the AcOH soln. is treated in ice with Na_2CO_3 1 mol. HBr is split off and there is pptd. a red granular *compound*, $C_{20}H_{15}N_2Br$, very unstable, sensitive to light, gives in alc. with acids a blue dye which again becomes colorless in excess of acid and is likewise very unstable, as is the cryst. *picrate* of the red compd. The blue dye has a band at about 560$\mu\mu$. If, after the Br titration, more Br is added there finally seps. a yellow *substance*, possibly a perbromide $C_{20}H_{16}N_2Br_4$ (found, 55.2% Br). When IV is heated 1–2 hrs. on the H_2O bath with an

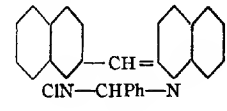


excess of Me_2SO_4 and the resulting almost colorless addition product is converted into the colored monomethosulfate by soln. in alc., freed from any unchanged IV by addition of H_2O, treated with KI and KOH, warmed and treated with more KI, there is obtained 80–5% pseudoisocyanine (B), identical with the natural product in appearance, cryst. form, color, soly. and extinction coeff. differences for different wave lengths, and yielding the same picrate. S., however, does not consider that this establishes the structure V which had been assigned to B (*C. A.* **14**, 3636), but which does not account for the firm union of the halogen, so characteristic of the cyanines. Moreover, while II and B show 2 absorption bands at the same positions, IV shows only end absorption.

This difference may possibly be due to the possibility of oscillation in the case of II and B. If it is assumed that quinoline red (C) has a structure (VI) analogous to that given by Vongerichten to isoquinoline red (*C. A.* **7**, 2319), C should result from the action of $PhCHCl_2$ on A; as a matter of fact, C is obtained in 20–40% yield from A heated 0.5 hr. on the H_2O bath with an excess of $PhCHCl_2$ and then heated with an equal vol. of C_5H_5N in a sealed tube at 150–60° until the color has changed to dark violet, treated with alkali, distd. with steam, filtered hot and pptd. with HCl.



V



VI

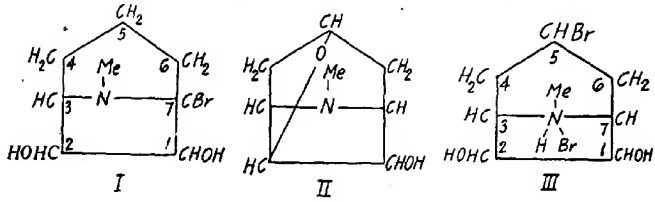
CHAS. A. ROUILLER

Asymmetric rearrangement. HERMANN LEUCHS. Univ. Berlin. *Ber.* **54B**, 830–4(1921); cf. *C. A.* **7**, 3330.—If hydrocarbostyril-β-carboxylic acid (A) has the ketonic structure $CO.NH.C_6H_4.CH_2.CHCO_2H$, it should be resolvable into optical antipodes. As a matter of fact, when 2.4 g. of the synthetic *dl*-acid and 4.07 g. quinidine (dried at 100°) in 40 cc. hot MeOH are cooled in ice there seps. 4 g. of long needles and concn. of the mother liquor yields 2.2 g. more, m. 138–46° (gas evolution), having the compn. $C_{20}H_{24}O_2N_2.C_{10}H_9O_2N.2H_2O$, m. 138–40° (loss of CO_2) when dry, and yielding with 5 *N* HCl at −10° 85–95% of the free acid, m. 145–6° (loss of CO_2), showing $[\alpha]^0_D$ in 3.5% soln. in AcOH in a 0.5 dcm. tube 1.08° after 0 min. and decreasing according to a monomol. reaction to 0.11° after 120 min.; at this point the thick 4-sided tables of the *dl*-acid, which are difficultly sol. in AcOH, began to sep., but the filtrate still showed a rotation of 0.08° owing to the presence of a little quinidine-HCl which cannot be removed from the *d*-A by washing with H_2O or even with 5 *N* H_2SO_4; the *d*-A can be obtained pure, however, by dissolving in 10 parts cold AcOH and immediately pouring into 30 parts ice H_2O; it forms needles or prisms with 1 H_2O, sol. clear in $NaHCO_3$, m. 145–6°, $[\alpha]^{18}_D$ 56.4° (AcOH). This complete conversion of a *dl*-compd. into the *d*-form with total disappearance of the *l*-antipode is explained by the mobility of the H on the asym. C atom, produced by the proximity of the enolizable keto group. If the salt of the *d*-keto acid, present or formed from the enol, crysts. out, only the salt of the *l*-keto acid can be enolized, but the enol salt can be ketonized only to the *d*-salt, for the equil. *l*-acid salt (⇌) enol acid salt (⇌) *d*-acid salt ⟶ crystals is always shifted in favor of the *d*-salt, as this crysts. out. The conversion of the *l*- into the *d*-form therefore does not take place through the racemic compd. but through a compd. without an asym. atom which by rearrangement yields one of the antipodes exclusively. This case therefore does not fulfill the conditions for a so-called "asym. synthesis" only in that the mol. wt. remains unchanged, and L. therefore designates this reaction as an "asym. rearrangement." CHAS. A. ROUILLER

β-Hydroxy-β-3,4-methylenedioxyphenylethylamine and its derivatives. FREDERICK ALFRED MASON. *J. Chem. Soc.* **119**, 1077–81(1921).—This work was undertaken for the purpose of synthesizing 6,7-methylenedioxyisoquinoline from $CH_2O_2C_6H_3CHO$ through the cyanohydrin, the hydroxyamine and the formyl deriv. The work was abandoned at the formyl deriv. *β-Hydroxy-β-3, 4-methylenedioxyphenylethylamine* was prepd. essentially according to Eng. pat. 27,117(1907). *Hydrochloride*, $C_9H_{11}NCl$, prismatic crystals, m. 176°. *Formate*, $C_{10}H_{11}O_4N$, m. 138–9°. *Chloroplatinate*, brilliant orange scales, decomp. above 170–200°. *Urethan*, $C_{12}H_{14}O_4N$, m. 105°. *Benzoate*, $C_{16}H_{15}O_4N$, glistening leaflets, m. 155–7°. *p-Nitrobenzoate*, $C_{16}H_{14}O_6N_2$, small, yellow

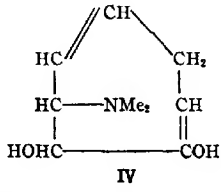
leaflets, m. 155–7°. *Di-p-nitrobenzoate*, $C_{22}H_{17}O_8N_3$, small orange yellow crystals, m. 179–80°. *Veratroyl derivative*, $C_{18}H_{19}O_5N$, friable resinous mass, m. 60–80°. *Formyl derivative*, $C_{10}H_{11}O_4N$, prepd. by boiling the base with formic ester, m. 90–2°. It is believed that the desired synthesis may be carried out by Pictet and Gam's method (*C. A.* **4**, 3222). C. J. WEST

Scopoline. J. GADAMER AND F. HAMMER. *Arch. Pharm.* **259**, 110–35(1921).—The authors present a brief review of previous work relative to the constitution of scopoline, notably Hess's expts. (cf. *C. A.* **13**, 591) on the Hofmann degradation of this base. Partly on account of apparent contradictions in Hess's theory as related to his exptl. findings, and for other reasons, G. and H. have undertaken the work described below. Shortly after its inception, however, the sepn. of inactive scopoline by means of *d*-tartaric acid into its components was reported by King (cf. *C. A.* **13**, 2012). Accordingly, active scopoline was chosen as the initial starting point for the investigation. To this end *l*-scopoline, $[\alpha]_D$ −52.3°, was treated in a bomb tube at 125–7° with HBr in AcOH, whereby *l*-scopoline-HBr, $C_8H_{13}NO_2.HBr$, identical with that formed by neutralizing the base with HBr, together with inactive hydroscopoline bromide-HBr, $C_8H_{14}BrNO_2.HBr$, resulted. This fact is important in that it tends to disprove the constitutional formula as advanced by Hess. If the arrangement of the Et_2O-like O atom of scopoline exists as this investigator claims, then an optically active *l*-hydroscopoline bromide-HBr must be formed on cleavage of the O-bridge and addition of HBr, in that the Br unites either with the 7- or 2-C atom, with the simultaneous formation of an OH group at position 2 or 7 (formula I). In either case, an asymmetric compd. would result in accordance with Hess's formulation, which demands optical activity. The formation of an inactive deriv. as above stated is explainable only in the event that the O-bridge is so situated in the mol. as to permit the formation of a sym. compd. on cleavage of the bridge and addition of HBr. This is possible only in case

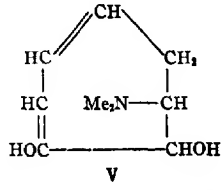


the O-bridge formation in question is assumed as taking place between C atoms 2 and 5 (II), while in the ring cleavage Br unites at 5, OH at position 2. That the latter group is in fact held by this C atom has already been shown by Schmidt in the oxidation of hydroscopoline to N-methyl-α,α_1-piperidinedicarboxylic acid. *l*-Hydroscopoline bromide-HBr has therefore the constitution (III). The influence of the 4 asym. C atoms contained therein, (1, 2, 3 and 7) is inhibited through intramol. compensation, in that the H atoms at 3 and 7 as also the HO groups at 1 and 2 are in the *cis*-positions. These considerations indicate with reasonable certainty that the O-bridge in the scopoline mol. exists between the C atoms 2 and 5. Additional proof is yielded by the Hofmann degradation. Thus, *d*-scopoline is made to yield *via* the methiodide and the quaternary ammonium base 2 isomeric bases, the pseudo-des-methylscopolines of Hess, which differ in b. p. optical rotation and crystal form. Both isomers are unsatd. compds. containing 2 double bonds. The formation of these bases, unintelligible when regarded from the standpoint of Hess's formula, may be explained if scopoline is formulated in a manner similar to that ascribed to *l*-hydroscopoline bromide-HBr. Assuming for *d*-scopoline the optical function of the asym. C atoms 1, 2, 3 and 4 as in the formula

in which C_1 is *l*-rotatory if 2 rotates to the right, C_7 *d*-rotatory if 3 rotates to the left, it follows that, in the Hofmann degradation, N cleavage could result both at C_7 and C_2, the O-bridge simultaneously suffering cleavage through the intermediary addition and splitting off of H_2O, thus yielding the 2 compds. IV and V. These are, on account of the double bond between

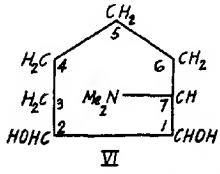


IV

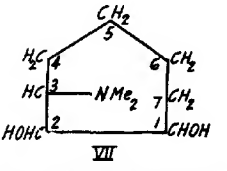


V

4 and 5, diastereomeric, not enantiomorphous. The position of the double bonds affords a satisfactory explanation for *l*-rotation, stability and ability to cryst. This formulation is also in harmony with the fact that only one OH group can be detected in pseudodesmethylscopoline, on account of its ability to ketonize. That the presence of C:O is not susceptible of proof in such cases is illustrated in the protopine group. On hydrogenation *via* Paal-Skita, each base yields 2 tetrahydro compds. formulated in VI and VII, this reduction changing C_1 and C_2 (shown in IV and V, resp.), into the asym. form.

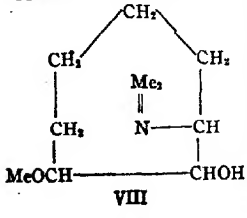


VI



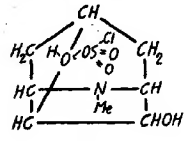
VII

There are thus 3 asym. C atoms, which permit the existence of 8 optically isomeric forms, of which 4 from *d*- and 4 from *l*-scopoline were actually obtained. In studying the effect of the Hofmann degradation on the tetrahydropseudodesmethyl-*d*-scopoline bases, it was found, in harmony with Hess's experience, that the sepn. of Me_3N, which might reasonably be expected, occurred only in very small measure. Migration of Me to one of the 2 OH groups takes place, as shown by the Zeisel detn. The bases so obtained are optically active oily liquids, which while fairly stable become colored in a short time. The formation of these *O*-methylated bases may be explained as follows. The quaternary NH_4 base tends to pass into a tertiary base on heating. The OH ion becoming thus available reacts with the favorably situated secondary alc. group to yield a mol. of H_2O. As this sepn. of H_2O progresses, a simultaneous migration of the Me group to the free valence of the hydroxyl O takes place. Thus the MeO group finally appears at C_2 (formula VIII). Other expts. calcd. to throw light on the constitution of scopoline consisted in the treatment of the active base with $ClSO_3H$. The oxonium compd. first formed (formula IX) becomes X through mol. rearrangement, the latter thereupon forming an inner salt (XI) on contact with ice, which should accordingly have a neutral reaction. The product obtained, however, possessed an acid reaction due to the presence of a minute quantity of a diethereal sulfate, which resulted from the esterification of the OH group at C_1. On subjecting the product of the action of

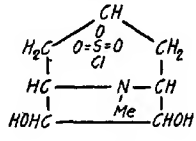


VIII

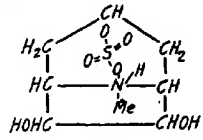
$ClSO_3H$ on active scopoline to hydrolysis, optically active hydroxyhydroscopoline, $C_8H_{13}NO_3$, was obtained, which may be regarded as isomeric with the teloidine of Pyman



IX

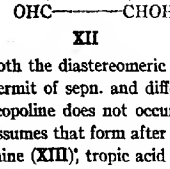


X



XI

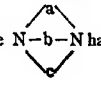
and Reynolds (cf. *C. A.* **3**, 883), and having the constitution shown in **XII**, although this formulation presupposes a Walden rearrangement resulting from the action of $ClSO_3H$ on C_2, in that both hydroxyls assume the *cis*-trans position at C_1 and C_2, thus producing asymmetry of the mol. and consequently optical activity. Attention is called to the apparent lack of any satisfactory explanation of the fact that natural *l*-scopolamine yields on hydrolysis *l*-tropic acid and *dl*-scopoline. King as well as the present authors have shown that scopolamine is resolved into active components, and that both the diastereomeric compds. *d*-scopoline *l*-tropate and *l*-scopoline *l*-tropate do not permit of sepn. and differentiation. In this connection the assumption is made that scopoline does not occur in the scopolamine mol. in the form represented by **II**, but assumes that form after hydrolysis. In the commonly accepted formula for scopolamine (**XIII**), tropic acid is in ester combination with the base at C_1. There is still the



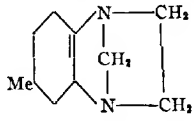
XII

possibility that union is made at C_4, in which event scopolamine would assume the sym. form expressed in **XIV**. In the sepn. of scopoline from such a combination by hydrolysis, a simultaneous cleavage in the C_2H_4O group would be effected with the formation of a new O-bridge between C_3 on the one hand and C_1 or C_2 on the other. The resulting base would be *d*-scopoline. An expt. with scopolamine and HBr in AcOH failed to yield any satisfactory proof of the above assumption since similar results were obtained as reported for scopoline. Further expts. along this line are promised.

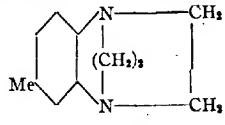
W. O. E.

Some new tricyclic bases. Tom Sidney Moore and Ida Doubleday. Royal Holloway College. *J. Chem. Soc.* **119**, 1170–5(1921); cf. *C. A.* **9**, 2892.—Three compounds of the type  have been prepd. *1,4-endo-Methylene-6-methyltetrahydro-*

quinoxaline (I), prepd. by heating 6-MeC_6H_3:$(NHCH_2-)_2$ with $(HCHO)_3$ for 2 hrs., extg. the product with H_2O and then with C_6H_6 and pptg. with petr. ether, or better by using CH_2I_2 at 100° for 4 hrs., pptg. the base with NaOH and purifying as above, faintly brown, decomp. 150°, sol. in glacial AcOH and dil. mineral acids with red color. *Hydrochloride*, $C_{10}H_{12}N_2$.HCl, colorless. *Dihydrochloride*, reddish brown. *Normal oxalate*, reddish brown hygroscopic solid. *Acid oxalate*, by slow addition of the powdered base to the calcd. quantity of $C_2H_2O_4$ in hot alc., yellowish brown, very hygroscopic solid, giving a purplish red soln. in H_2O, reddish brown soln. in AcOH. *Methiodide*, reddish brown, decomps. 118–20°. *Dimethiodide*, by heating the base at 130° for 6 hrs. with excess MeI, yellowish brown, very hygroscopic solid, decomp. 101°. The soln. is reddish brown in H_2O, greenish brown in alc., and red in PhOH. *1,4-endo-Ethylene-6-methyltetrahydroquinoxaline* (II), decomp. 175°. *Hydrochloride. Dihydrochloride. Oxalate. Acid*



I



II

oxalate. 1,4-endo-Trimethylene-6-methyltetrahydroquinoxaline, $C_{12}H_{16}N_2$, decomp. 192°. *Hydrochloride. Dihydrochloride. Oxalate. Acid oxalate.* The colors are similar to those given for I. C. J. WEST

Influence of double bonds on the coördination number (PIERONI) 6. The catalytic action of salts of some metals in the reactions of organic compounds (KORCZYNSKI) 2. Catalytic dehydrogenation of alcohols (RIDEAL) 2.

BERNTHSEN, A.: **Kurzes Lehrbuch der Organischen Chemie.** Friedr. Vieweg & Sohn. 696 pp. bound M 15. For review see *Tonind.-Ztg.* 45, 697(1921).

WEST, AUGUSTUS, P.: **Experimental Organic Chemistry.** London: George G. Harrop, 293 Portsmouth St., Kingsway, W. C. 469 pp. 10s 6d net.

Maleic acid. J. M. WEISS and C. R. DOWNS. U. S. 1,377,534, May 10. Maleic acid, benzaldehyde and benzoic acid are produced by oxidizing toluene vapor with air at a temp. of 400–550° with the use of V oxide as a catalyst.

Trinitroresorcinol. W. FRIEDERICH. Brit. 162,578, July 2, 1920. Trinitroresorcinol is obtained by nitrating resorcinoldisulfonic acid, suspended in concd. H_2SO_4, with HNO_3 of 90–100% at a temp. of 30–80°. According to an example, powdered resorcinol is sulfonated with an excess of concd. H_2SO_4 at 70° and HNO_3 of 48° Bé. slowly added to the reaction mixt. at a temp. of 50°.

11—BIOLOGICAL CHEMISTRY.

HATTIE L. HEFT, EDGAR G. MILLER, JR., AND WILLIAM J. GIES

A—GENERAL

FRANK P. UNDERHILL

Nuclein metabolism. X. Deaminization of triphosphonucleic acid. S. J. TANNHAUSER AND P. SACHS. *Z. physiol. Chem.* 112, 187–192(1921); *J. Chem. Soc.* 120, I, 201.—The mixt. of acids (triphosphonucleic acid and mononucleotides) obtained by mild ammoniacal hydrolysis of yeast-nucleic acid was deaminized by treating the mixt. dissolved in AcOH with $NaNO_2$, neutralizing and pptg. with Pb acetate. The Pb

compd. was decomposed by H_2S, filtered, the filtrate concd. in a vacuum, and pptd. by alc. By treatment with brucine and fractional crystn. 2 crops of crystals were obtained, m. 189–190° and 194–195°, resp., but these gave on analysis identical figures corresponding with those required for the brucine salt of a diaminotriphosphonucleic acid. The pure triphosphonucleic acid was deaminized in the above way, and the brucine salt prepd. from it melted at 185°. Adenosine phosphoric acid could not be deaminized without being decomposed. H. V. ATKINSON

Studies on the action of poisons. The action of quinine on serum lipase. PETER RONA AND DORA REINICHE. *Biochem. Z.* **118**, 213–31(1921).—A study is reported of the effect of quinine on the serum lipase activity of serum from man, rabbits, cats, rats, mice and guinea pigs. The reactions were buffered by phosphate mixts. and tributyrin was the substrate. The results demonstrate that the inhibitory action of quinine-HCl on serum lipase is of the same type as occurs with atoxyl (Rona and Bach, *C. A.* **15**, 1763). The toxicity is directly proportional to the log of the concn. of the poison. No protective action of tributyrin was observed. The inhibitory action of the quinine salt increases with increasing alkalinity. This also occurs with different quinine salts. A peculiar fact is brought out that the compd. acts as a toxic substance in serum from animals only when present in concns. 100 to 1000 times as great as are effective in human serum. When human and animal sera are mixed no protective action of the latter is observed; but the lipases work individually with additive result. If atoxyl is combined with quinine, the former is retarded from acting on the enzyme if the latter is added first. But if the atoxyl is allowed to remain with the enzyme for a longer period there is observed an additive effect in the majority of cases. F. S. HAMMETT

Studies on the action of poisons. The action of *m*- and *p*-nitrophenol on invertase. PETER RONA AND EMERICH BACH. *Biochem. Z.* **118**, 232–53(1921).—The toxic action of *m*- and *p*-nitrophenol on invertase is not immediate but extends over a considerable period. This toxic action has a distinctly rising value. For *m*-nitrophenol this is at a concn. of 0.6 mols. per l. for *p*-nitrophenol at 0.04 mols. per l. Above these values the retardation action is proportional to the concn. of the compd. studied. The concn.-inhibition curve then takes practically a straight-line course. The range of toxic action is narrow, a doubling of the effective concn. results in total inhibition. The process is not reversible nor was any influence of the H-ion concn. noticeable. Temp., however, had a marked effect. The temp. coeff. was 1.87. F. S. HAMMETT

Comparative investigation of the corresponding proteins of cow and ox serum, cow colostrum and cow milk by the method of protein racemization. H. E. WOODMAN. Cambridge Univ. *Biochem. J.* **15**, 187–201(1921).—The method has its basis in the observation of Kossel (*C. A.* **5**, 3572; **7**, 91, 2229) and Dakin (*C. A.* **7**, 489) that when solns. of protein in dil. NaOH soln. are kept at 37°, they suffer a progressive diminution in the value of their optical rotatory power. Dakin attributed this change to a keto-enol tautomerism in the protein complex, and showed that the optical characters of the individual amino acids obtained by hydrolysis of a racemized protein afford information as to their situation within the original protein mol. Using the "racemized" method, Dudley and the author (*C. A.* **9**, 1623) detected structural differences in the amino-acid make-up of the caseinogens of the cow and the sheep, and showed that the euglobulin and pseudoglobulin of cow colostrum were identical (*C. A.* **13**, 1495). Similarly, Dakin and Dale (*C. A.* **14**, 767) have shown structural differences to exist between the albumins of the eggs of the duck and the hen—a result recently confirmed by biological tests. W. has materially simplified the racemization process in the following way: If, for example, the $[\alpha]_D^{37}$ of a 2% soln. of globulin in 0.5 *N* soda be plotted against the time in hrs. the readings fall on a perfectly smooth curve. On the assumption that each individual protein will possess its own sp. set of curves, the racemization reaction

can be made the basis of a method for testing the identity or non-identity of proteins. By such means W. shows that euglobulin and pseudoglobulin fractions in both serum and colostrum contain identical proteins; that serum globulin is identical with colostrum globulin; that no differences can be detected between the corresponding proteins of cow and ox serum; that the albumins of milk and colostrum are identical; that lactalbumin and serum albumin have been shown to be distinct chemical individuals. This last result would appear to indicate that not only is a distinct mammary synthesis necessary for the formation of caseinogen, but also for synthesis of lactalbumin; and that the hypothesis, which assumes that the lactalbumin is obtained by a mere transfer of serum albumin from the blood to the gland, will have to be discarded. The proteins from different sources were prepd. by the use of the same methods. The total globulin was removed from neutral soln. by half-satn. with $(NH_4)_2SO_4$; the pseudo and euglobulins were sepd. by dialysis. The albumin was obtained from the filtrate from the total globulin by the addition of the requisite vol. of 0.2 *N* H_2SO_4 together with an equal vol. of satd. $(NH_4)_2SO_4$, in order to maintain half-satn. The albumin was freed from $(NH_4)_2SO_4$ by dialysis. The samples of protein were fractionally pptd. 7 times, and in order to be sure that further pptn. would not affect the optical behavior of the protein in dil. alkali, portions of protein from the 6th and 7th fractionations were racemized separately. In this way it was possible to obtain a check on the completeness of the sepn. of the albumin from the globulin. The racemization method was carried out as follows: the samples of proteins were finely ground up and dried *in vacuo* over $CaCl_2$ for several days. One g. of dried protein was weighed out into a 50-cc. flask contg. a little distd. water. The flask was shaken gently to bring the protein into soln. or suspension. 25 cc. of *N* NaOH free from carbonate were run from a pipet, and after gentle mixing the vol. was made up almost to the 50-cc. mark with distd. water. The flask was placed in the incubator at 37° and after the contents had become warm, the vol. was made up exactly to the 50-cc. mark. After a short time the soln. was filtered into a small dry flask, which was stoppered and kept in the incubator. From time to time detns. of optical activity were made in a 1-dm. polarimetric tube, with a Schmidt and Haensch instrument and sodium light. This was continued for 300 hrs. when the value had become practically const. BENJAMIN HARROW

Influence of reaction on color changes in tryptophan solutions. E. C. V. MATTICK AND R. S. WILLIAMS. Univ. Coll., Reading. *Biochem. J.* **15**, 213–215(1921); cf. Cornish and Williams, *C. A.* **11**, 3295, and Venn, *C. A.* **14**, 2007. The organism used was *B. proteus vulgaris*. Colors were produced with tryptophan when the solns. inoculated ranged in p_H value between 8.9 and 9.4. BENJAMIN HARROW

Relation between the number and size of red corpuscles and the opacity of their suspensions. J. HOLKER. *Biochem. J.* **15**, 226–231(1921).—"Endosmosis and exosmosis can be measured by means of the opacimeter (cf. *C. A.* **15**, 3120). By plotting the results of endosmosis and exosmosis the isotonic point can be accurately detd. The opacity-concn. curve of a suspension of red corpuscles is a straight line with the equation $T = k\,C$, where T = opacity, C = concn. of corpuscles per cm., and k = const., which varies with the animal, and is a measure of the size of the red corpuscles. The av. size of mammalian red corpuscles can be detd. from the equation, diam. $= 2.402 \times 10^3/\sqrt{CD}$, where C = number of cells per cm., and D = opacity reading. The diam. of the corpuscle is inversely proportional to the square root of the product of the cell count and opacity reading. The opacity const. k for any given mammalian red corpuscle, that is, the theoretical turbidity produced by one such corpuscle per cu. mm. of suspension, can be detd. from the equation, $K = 0.171d^3 \times 10^{-4}$, where d is the diam. of the corpuscle. The opacity of a suspension of red corpuscles is a measure of the total surface of the suspended particles. BENJAMIN HARROW

Relation between the microscopic appearance of precipitated calcium oxalate and the opacity of its suspensions. J. HOLKER. *Biochem. J.* **15**, 232–237(1921).—Measurements were made by means of the opacimeter (cf. *C. A.* **15**, 3120). When dil. solns. of $CaCl_2$ and $K_2C_2O_4$ are brought together there is a lag before any turbidity appears; in concd. solns. there is a period of oscillations of the turbidity, before equil. is established. The turbidity curve for equil. turbidities shows a short initial flat lag, a longer intermediate zone of increasing steepness, and a long final zone of diminishing steepness. A first "critical point" in the intermediate zone represents the point at which the crystals have attained a size at which they do not tend to redissolve; a second "critical point" represents the point at which the crystals reach their max. size. Beyond this point the crystals diminish in size but increase in number. Excess of either oxalate or Ca ions increases the opacity. BENJAMIN HARROW

Opacity of serum diluted with distilled water, physiologically normal saline, and Ringer solution. J. HOLKER. *Biochem. J.* **15**, 238–243(1921); cf. preceding abstract. —Serum was used which had been "inactivated" by heating at 56° for 20 minutes. From the inactivated serum was prepd. a series of dilns. in Jena glass test-tubes, which were then allowed to stand for 4 hrs. at 40°, but were shaken every hour. Whether the serum is normal or pathol., or whether it is dild. with distd. water or with salt soln., the turbidity-concn. curve is not a straight line such as is produced in dilg. a suspension of red corpuscles, but that for all dilns. the turbidity is greater than that which would be produced if the protein particles scattering the light had remained the same in size and had merely been proportionally reduced in number. The significance of such a result, particularly in pathol. cases, is discussed. Evidence is deduced that the *Wassermann reaction* depends on surface action. BENJAMIN HARROW

An autoxidizable constituent of the cell. F. G. HOPKINS. Biochem. Lab., Cambridge. *Biochem. J.* **15**, 286–305(1921).—A suggestive paper in which is described the isolation from yeast, muscle and mammalian liver of the substance in the cell that gives the nitroprusside test. This substance, a dipeptide contg. glutamic acid and cysteine, is probably identical with the "philothion" of de Rey-Pailhade (*Compt. rend.* **106**, 1683; **107**, 43(1888)). H. proposes the name *glutathione* for it "because it leaves a link with the historic *philothion*, has the same termination as *peptone*, which has long served as a name for the simpler peptides, and is a sufficient reminder that the dipeptide contains glutamic acid linked to a S compd." Evidence is presented to show that *glutathione* takes an active part in cell oxidations and reductions in the sense—SH HS $\rightleftarrows$ —S—S— $+H_2$. The actual isolation of the substance is a tedious matter. It is based on the soly. in water of the glutathione, and subsequent fractional pptns. BENJ. HARROW

Some problems in the biological action of radiations. S. RUSS. *J. Röntgen Soc.* **16**, 134–9, 139–41(1920); *Science Abstracts* **24A**, 304.—A table is given illustrating the general effects of heat, light ultra-violet rays, X-rays, and γ-rays on chem. reaction, photographic reaction, electronic emission, biol. reaction and physiol. reaction. The dependence of tissues, in their reaction to X-rays, upon the particular prevailing condition of physiol. mitosis is pointed out. The disagreement of expts. *in vitro* and *in vivo* is illustrated by expts. regarding the decrease of lymphocytes in the blood of the rat when exposed to X-rays, while on the other hand consistent results can be obtained in similar expts. regarding the effect of radium β-rays on rat sarcomata. The author suggests an explanation of these differences on the ground that the seat of the reaction is extracellular in the first case and intra-cellular in the second case. Selective and differential responses to the action of rays upon the same histological tissues are possibly due to a different stage in the life cycle. The final section is a very suggestive discussion of the relation between degree of biol. action and the absorbed energy of the radiation, which bears no simple relation and would appear to be due to the energy liberated from the

tissues by the radiations; it is particularly pointed out that those rays which give rise to the most striking biol. reactions also cause marked electronic emission. F. P. P.

The physico-chemical explanation of the changes in the nuclear substance. JOSEPH SPEK. Heidelberg. *Arch. Entwickl. Organ.* **46**, 537–46(1920).—This is an essay on the cell nucleus with special consideration of the work of Paolo Della Valle (*Arch. zoöl. italiano* **6**, 37–321(1912)). The subject is discussed under the following headings: Prophase; appearance, number and size, state of aggregation and consistency, form, colorability, optical properties and cataphoresis of the chromosomes; metaphase; splitting of the chromosomes; telophase. The colloidal chem. nature of the cell nucleus is emphasized. The discussion is based upon the existing literature; no new expts. nor observations are included. CHAS. H. RICHARDSON

Synthesizing action of α-methyl-*d*-mannosidase. H. HÉRISSEY. *Compt. rend.* **172**, 1536–9(1921); cf. *C. A.* **15**, 1733—Mannose was prepd. by the decompn. of mannose phenylhydrazone by means of C_6H_5COH and recrystn. of the product from EtOH. Three solns. were made up: *A* containing 0.9622 g. of mannose, MeOH (99.5%) 10g., water up to 100 cc., enzyme powder from seeds of lucerne 4 g. and toluene 1 cc. *B* was like *A* with the enzyme omitted and *C* like *A* with the mannose omitted, *B* and *C* serving as controls. These mixts. were allowed to stand 6 days at lab. temp. with agitation at least once a day. Portions of 20.3 cc. were withdrawn, defecated with 1 cc. basic lead acetate soln. and both rotatory and reducing powers detd. There was a progressive increase in rotatory power and a correlative decrease in reducing power. Exts. were obtained from the fermenting mixt. which gave crystals upon inoculation with α-methyl-*d*-mannoside that showed all the characteristics of the latter. L. W. RIGGS

The microscopic forms of iron rust (ACKERMANN) **2.**

BENNETT, H. G.: Animal Proteins. London: Baillière, Tindall & Cox. 287 pp. 15s.

MASSART, JEAN: Eleménts de biologie générale et de botanique. **Vol. 1, Pt. I.** Bruxelles: Maurice Lamertin. 208 pp. For review see *Botan. Abstracts* **7**, 303(1921).

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Preparation of isotonic solutions. FRANCESCO NICOLA. *Giorn. farm. chim.* **70**, 57–63(1921).—To calc. the concn. of a given substance required for a soln. approx. isotonic with blood serum (0.95% NaCl) N. uses the formula $p=0.302\ m/i$, where p=g. per l. required to make an isotonic soln., i=dissociation coeff. and m=mol. wt. of the substance. For practical purposes the following values can be substituted for i: 1 for nonelectrolytes and 1.5, 2.0, 2.5, resp., for electrolytes which dissociate into 2, 3, 4 ions. For an isotonic soln. of sucrose, *e. g.*, $m = 342$ and $i = 1$; therefore $p = (0.302/1)\times342 = 103.28$ g. per l. To render a soln., *e. g.*, 1% cocaine-HCl($m = 339.5$, $i = 1.5$), isotonic by addition of NaCl ($m = 58.5$, $i = 1.86$) the calcn. is $(10/339.5) \times 1.5 = 0.0441$ and $(0.302-0.0441)/1.86\times58.5 = 8.1$ g. NaCl per l. Solns. for eye washes should be isotonic with the lacrymal secretion (1.4% NaCl, $i = 1.8$). The equation then becomes $p = 0.43\ m/i$. A. W. DOX

New method for the preparation of the medullary sheath (of the neurokeratin) and of the axis cylinders. H. MÜLLER. *Z. wiss. Mikros.* **36**, 147–56(1920); *Physiol. Abstracts* **5**, 175.—It was found that fixation with $CaCl_2$ was very convenient if it was wished to apply the Weigert medullary-sheath stain to paraffin sections. The exact procedure is described. For selective staining of the neurokeratin with hematoxylin, Cu sulfate can be used as a mordant with good results, and similarly Cu acetate for axis cylinders. H. G.

Methods of measuring the opacity of liquids. J. HOLKER. Univ. of Manchester.

Biochem. J. **15**, 216–225(1921); cf. Don and Chisholm, *Methods of Water Purification*, p. 273(1911), and Gates, *J. Exp. Med.* **31**, 105(1920).—The original app. consisted of a loop, such as is commonly employed in bacteriol. subcultures, which was bent at the end of a wire at a right angle and the shaft was fixed to a sliding micrometer provided with a scale and vernier. In this way the depth of the loop below the surface of the emulsion at which it just disappeared from sight could readily be detd. An improved form of the app., called an "opacimeter," was one where the wire was fixed in a const. position, while the depth of the liquid under examn. was made to vary. Still another modification is described to meet the requirements such as those that arise in serum reactions, where the amount of material is strictly limited. BENJAMIN HARROW

The theory of the Barcroft differential blood-gas apparatus. T. R. PARSONS. Physiol. Lab., Cambridge. *Biochem. J.* **15**, 202–208(1921).—"During the course of a lengthy series of investigations in which the Barcroft differential app. has been used for blood-gas measurements a certain number of results were encountered which seemed to suggest that the evolution of a given vol. of gas in one of the bottles of the app. might give rise to a somewhat smaller difference of level on the clove-oil manometer than the absorption of an equal vol. of the gas from the same bottle under similar conditions. In other words, it seemed possible that the value of the const. of the app. might not be identical for the two cases of evolution and absorption of gas." This is now shown not to hold. The exptl. result is compared with that which might be expected if the mathematical theory of the differential app. is applied. BENJAMIN HARROW

A system of laboratory examinations and records. JOHN A. KOLMER. Univ. Penn. *J. Lab. Clin. Med.* **6**, 505–19(1921).—The original must be consulted for details and charts. E. R. LONG

A modification of the technic of the vividiffusion method of Abel. H. C. VAN DER HYDE AND WITHROW MORSE. W. Va. School of Med., Morgantown. *J. Lab. Clin. Med.* **6**, 520(1921).—The principal difficulty with the method as first suggested has been in the prepn. of the dialyzing tubes. The following method is suggested: A glass rod slightly larger than the diam. of the tubes of the app. is dipped a decimeter into liquid collodion. A piece of fish bladder tissue 12 cm. long and 1.5 cm. wide is wrapped around the tube, extending 2 cm. beyond the end, so that it can be removed by pulling on this extension. The cylinder is slipped off before the collodion has set to the point of adherence to the rod. The cylinders can be dried by clamping them in a vertical position or pinning them to the sides of the table. E. R. LONG

Reaction of Adamkiewicz. Condensation of α-methylindole with glyoxylic acid. G. PLANCHER. *Giorn. chim. ind. applicata* **2**, 459(1920).—The reaction of Adamkiewicz, *i. e.* production of a green ring when com. AcOH and concd. H_2SO_4 react upon a protein, has been shown to be due to the presence of glyoxylic acid in the AcOH. P. endeavored to confirm this. He treated 20% aq. soln. of glyoxylic acid, to which HBr was added, with 20% alc. soln. of methylketole. Superposing the 2 solns., a cryst. compd. sepd. in the course of 2 hrs. This, collected and rapidly crystd. from boiling alc., turned slightly reddish, but collected upon a plate and washed with alc. it remained a beautiful white. It becomes brown at 180°, m. 208–9°, with evolution of CO_2, and corresponds to the formula $C_{10}H_{13}N_2O_2$. It is an acid that decomposes alk. carbonates. Esterified by boiling for 3 hrs. in alc. soln. with $^1/_2$ mol. anhydrous K_2CO_3 and EtI, it gives an Et ether of the compn., $C_{22}H_{22}N_2O_2$. A dil. soln. of either of these 2 compds. in glacial AcOH mixed with pure concd. H_2SO_4 gives no color or a very slight orange yellow, at the junction of the 2 liquids. But the addition of a little very dil. soln. of H_2O_2 or Na_2O_2 brings about the characteristic Adamkiewicz coloration. Hence the Adamkiewicz coloration is due to the oxidation of the products of condensation of the indols with formaldehyde or glyoxylic acid. ROBERT S. POSMONTIER

Determination of dextrose and levulose in solutions (MURSCHHAUSER) 7. Evaluation of lecithin (MARCK) 17.

RUPP, E.: **Kurzgefasster Gang der chemischen Trinkwasser und Harnanalyse.** Stuttgart: Verlag der Süddeutschen Apothekerzeitung. For review see *Z. angew. Chem.* **34**, Aufsatzteil, 171(1921).

C—BACTERIOLOGY

A. K. BALLS

Glucose as a source of carbon for certain sweet potato storage-rot fungi. J. L. WEIMER AND L. L. HARTER. Bur. of Plant Industry. *J. Agr. Research* **21**, 189–210(1921). —Modified Czapek's culture solns. were prepd. to contain glucose in concns. from 0 to 60%. The following 8 fungi, which cause decay of sweet potatoes in storage, were grown at 28°, *Fusarium acuminatum, Diplodia tubericola, Rhizopus tritici, Mucor racemosus, Sclerotium bataticola, Penicillium sp., Botrytis cinerea* and *Sphaeronema fimbriatum*. The rot of mycelium was detd. by drying in a vacuum oven at 60°, the glucose content of the solns. was detd. by means of a Fric saccharimeter. The depression of the freezing point was detd. by a Beckman thermometer in a flask cooled by the evapn. of Et_2O and the osmotic pressure then calcd. The changes in acidity (p_H values) were made with a potentiometer according to Michaelis. Considerable variation in the amt. of glucose consumed by the different fungi at the same concn. was noted. The greatest glucose consumption was found in solns. of about 10% and decreased with the increase of concn. All but 2 of the fungi grew in solns. containing from 42 to 50% glucose. *Penicillium sp.* alone grew in 58% glucose soln. The different fungi produced varying amts. of dry mycelium at the same concn. and showed different concns. for the production of the max. amt. of fungous material and dry rot. The "economic coeff." of the different fungi varied. Three of the fungi had little influence on the H-ion concn., while 5 increased the acidity of the solns. All of the fungi grew in a soln. having a max. osmotic pressure varying from 81.33 to 101.46 atm. *Fusarium acuminatum* and *Mucor racemosus* increased the concn. and the other fungi generally decreased it. In general the decrease in osmotic concn. was not in proportion to sugar consumed; it is possible that compds. such as org. acids, EtOH, etc., were formed from the sugar, which would themselves influence the osmotic concn. F. C. COOK

Studies on Bacillus botulinus. PAUL F. ORR. Harvard Univ. *J. Med. Res.* **42**, 127–36(1921).—The toxins produced by 10 different strains of *B. botulinus* were found to be comparatively thermolabile. At 80° they are destroyed within from 30 sec. to 5 min., at 72° within from 2–18 min. and at 65° within 10–85 min. The heating of any food material to the b. p. will destroy all traces of botulinus toxin that might be present. The av. temp. coeff. of the destruction of the toxins on increasing the temp. from 65° to 72° was found to be 5.2 while on increasing the temp. from 72° to 80° the av. temp. coeff. was 4.2. E. B. FINK

Butyric acid and butyric alcohol fermentation. Recovery of acetaldehyde as a decomposition product. The transformation of "pyroracemic acid aldol" into butyric acid. The origin of higher fatty acids from sugar. CARL NEUBERG AND BERNHARD ARINSTEIN. *Biochem. Z.* **117**, 269–314(1921).—Up to the present the production of butyric acid from lipoid, protein and carbohydrate sources has not been satisfactorily accomplished. An extended discussion is presented of the mechanism of the reactions leading to this result. Equations are presented which demonstrate the butyric acid fermentation of sugar; the splitting of sugar into BuOH; the butyric acid fermentation from glycerol; and the process by which butyric acid and alc. can be derived from lactic acid. *Bacillus butylicus* Fitzianus was incubated in a nutrient soln. made up of 1 l. conductivity H_2O, 1 g. K_2HPO_4, 0.3 g. $MgSO_4$, 0.02 g. NaCl, 0.01 g. $FeSO_4$, 0.01 g. $MnSO_4$

and 0.50 g. $(NH_4)_2SO_4$ with a 2% glucose soln. alone and with $CaCO_3$, and with a 2% glycerol soln. alone and with $CaCO_3$. Other expts. are reported in which sucrose, invert sugar, maltose and starch were used. AcH was recovered. When "pyroracemic acid aldol" was added to the organism and incubated, butyric acid was recovered. When Na_2SO_3 is present, acetic acid is produced from the butyric acid instead of BuOH. In pure mineral salt soln. sugars are broken down by this organism and form higher fatty acids, *e. g.*, butyric, caproic, caprylic. F. S. HAMMETT

Studies on the bacteriology of the alimentary tract. N. MUTCH AND JANE MUTCH. *N. Y. Med. J.* **113**, 713–21(1921).—Glucophilia is a property peculiar to streptococci of alimentary origin and is almost universal among these organisms in the bowel. It may, therefore, serve as a criterion for the differentiation of streptococci of alimentary origin from other streptococci. The proportion of streptococcal strains at any point which possess extreme glucophilia increases progressively at successive intestinal levels from the mouth to the anus. The presence of carbohydrate is the most potent factor in the detn. of the dominance of the organism over *B. coli* at any level. Absolute suppression of *B. coli* by glucophilic streptococci takes place at a $p_H \approx 5.2$. The streptococci die at a p_H below 4.6. F. S. HAMMETT

Salt effect in alcoholic fermentation. ARTHUR HARDEN AND F. R. HENLEY. Biochem. Dept., Lister Inst. *Biochem. J.* **15**, 312–318(1921).—H. and H. corroborate Meyerhof's work (cf. *C. A.* **13**, 2056) by showing that in the fermentation of glucose and fructose by yeast juice or zymin (in the presence of phosphate), the chlorides and sulfates of Na and K exert a depressing effect on the max. rate attainable. As regards the effect in different stages of the process, chlorides and sulfates have no depressing effect on the rate of decompn. of pyruvic acid, while phosphates have a slightly stimulating effect, probably owing to the diminution of $[H^+]$ in their presence. The salt effect is not removed by the additions of acetaldehyde, but the salts decrease the rate of action of the hexose-phosphatase. The depressing effects produced by K_2SO_4 and by excess of phosphate differ in character, the latter being greatly diminished by addition of acetaldehyde, whereas the former is practically unaffected. BENJAMIN HARROW

Physiological chemical studies of the yeast cell. I. Use of the precipitometer and of the catalase apparatus to determine the course of fermentation. KARL SCHWEIZER. *Mitt. Lebensm. Hyg.* **11**, 193–200(1920).—The course of fermentation can be followed by detn. of the vol. of yeast cells (expressed in mm^3.) present in a given vol., *e. g.*, 1 cc., of the soln. undergoing fermentation. The vol. of the cells is detd. by mixing 1 cc. of the fermenting soln. and 0.5 cc. of 10% aq. soln. of Na_2CO_3 in the precipitometer, subjecting to 2000 r. p. m. for 5 min. in the centrifuge, and reading the vol. of the pptd. cells directly. The precipitometer is a centrifuge tube, and has an internal diameter of approx. 1 to 1.5 mm. at its narrow bottom portion which is so graduated that each scale division represents 1.5 mm^3. The growth curve of the yeast can thus be obtained by plotting the vol. of the yeast cells against the time in days. The course of fermentation can also be followed by placing a known vol., *e. g.*, 10 cc., of liquid medium in a suitable catalase app. such as that of Köstler, inoculating with a definite vol. of yeast suspension, and collecting and measuring the evolved CO_2 over water satd. with that gas. If the vol. of CO_2 produced be plotted against the time in days, the resulting curve differs somewhat, especially at the end, from that obtained by use of the vol. of yeast cells; this difference is due to the fact that the zymase continues to function and produce CO_2 after growth of the cells has ceased. **II. Application of the typical vitamine reactions upon the yeast cell.** *Ibid* 200–15.—The typical biological reactions for vitamines can be carried out with the yeast cell and a sugar soln. especially if a quant. detn. be made of the fermentation during the expt. Both autolyzed yeast freed from the cell membranes, and the membranes themselves, used separately, possessed an ex-

tremely small nutrient value for yeast, while their mixt. had the same value as the original product of autolysis. The mixt. had a nutrient value (measured by vol. of CO_2 produced by fermentation) which was 5 to 6 fold the sum of the nutrient values of its 2 components used separately. The autolyzed yeast decreased slightly in nutrient value for yeast when previously heated in an autoclave at a temp of 130° for 2 hrs. An aq. soln. of the alc. ext. of the press juice from autolyzed yeast, and an aq. soln. of the portion of the press juice insol. in alc., used separately, had but little nutrient value for yeast, in fact the sum of the vol. of CO_2 produced in these 2 expts. was but one-third to one-half that liberated when the entire product of autolysis was used. When yeast cell membranes were added to a fermenting soln. containing all the necessary ingredients, no distinct increase in fermentation occurred, while addition of the cell contents to such a soln. favored fermentation up to an optimum. The autoclaved autolyzed yeast had only a slight favoring action on fermentation under these conditions, and the alc. insol. fraction of autolyzed yeast exerted a retarding action. Addition of the aq. soln. of the alc. ext. increased the yield of CO_2 in proportion to the amt. added. These results do not confirm the existence of vitamines, for they may be due to the law of the minimum as deduced by Liebig for agricultural chemistry. Also in *Bull. assoc. chim. sucr. dist.* **38**, 163–71(1920). JOSEPH S. HEPBURN

The nature of the effect of blood pigment upon the growth of Bacillus influenzae. PAUL FILDES. London Hosp. *Brit. J. Expil. Path.* **2**, 16–25(1921).—The growth of *B. influenzae* has not been observed to occur in the total absence of blood pigment, though the quantity of blood pigment necessary is small. Probably oxyhemoglobin and carboxyhemoglobin are incapable of allowing growth, the feeble multiplication in these pigments being due to a spontaneous change to methemoglobin. Hematoporphyrin also fails to permit growth, but hematin allows a copious growth. *B. influenzae* on suitable media grows fairly well under anaerobic conditions, but rapidly dies out. The necessary O is obtained from an O store in the medium. This store is not dissolved active O, but is inactive in a state of loose combinations with a constituent of the medium. Under aerobic conditions the combined O is used up by the bacillus and immediately reformed from the atm. The combined O in the medium is activated for this bacillus by the catalytic action of Fe in the blood pigment. The feebleness of the growth on unchanged blood compared with that upon changed blood is due to a deviation of the O activated by the iron of the pigment from this bacillus through the O affinity of the unchanged pigment. HARRIET F. HOLMES

The question of serological races of V. cholerae and the relation of some other vibrios to this species. S R. DOUGLAS. Nat. Inst. Med. Research, London. *Brit. J. Expil. Path.* **2**, 49(1921).—The results show that all the strains of *V. cholerae* investigated belonged to one serological race, and as these strains came from widely different sources it is probable that there is only one serological race of *V. cholerae*. The advantage of using emulsions made by formolizing broth cultures, as recommended by Dreyer, when comparing the agglutinating properties of a series of strains of the same organism, is sharply brought out. After continued subculture on artificial media emulsions of *V. paracholerae* A acquired the property of being agglutinated by cholera-agglutinating sera, but these emulsions had no power of absorbing the agglutinins for emulsions of the homologous vibrio. This property was not lost either by repeated daily subculture in fluid media or by passage through a series of guinea pigs sufficiently numerous completely to restore the virulence of the organism. Of the El Tor vibrios, the strains known as A, 4 and 5 behaved both in their agglutinating and absorbing properties as true *V. cholerae*. Strain 10 behaved in an exactly similar manner to *V. paracholerae* A, being agglutinated by an antiserum prepared from this organism and absorbing the specific agglutinins from the *V. paracholerae* A antiserum. *V. nasik*, *V. paracholerae*

B and the El Tor vibrio 35 had no serological relation with either *V. cholerae* or *V. paracholerae* A. HARRIET F. HOLMES

The growth of the gonococcus in various gaseous environments. C. E. ROCKWELL AND C. F. M^{c}KHANN. Univ. of Cinn. *J. Infectious Diseases* **28**, 249–58(1921).—Cultures of the gonococcus isolated at partial tension by the aid of the hay bacillus grew under pure H_2 but not under CO_2 or O_2. When grown for some wks. under pure H_2 they seemed to become more sensitive to the deleterious influence of O_2 and CO_2, but still grew well by the partial tension method (hay bacillus). Although growth occurred under almost pure H_2, it failed when anaerobic conditions were produced by means of caustic soda and pyrogallic acid. Strains isolated at partial tension will not grow under pure O_2 or pure CO_2, but can be adapted to do so. It was noted during these expts. that the strains were able to adapt themselves to a new gaseous environment more rapidly than they lost old adaptations; *e. g.*, although a strain could be adapted to grow under CO_2 it required a prolonged series of subcultures under CO_2 to make it lose its ability to grow in the presence of O_2. A study of the delayed growth appearing in certain gas mixts. showed that an excessive supply of O_2 probably played an important part in producing the inhibition. This is supported by an analysis of the enclosed gases in a sealed culture, showing that growth begins after a certain amt. of O_2 is consumed and CO_2 given off. While moisture must play an important part, the expts. show that according to the previous gaseous adaptation of the microörganisms their growth will be favorably or unfavorably influenced by various gas mixts. All cultures, regardless of their adaptation, would grow under partial tension as furnished by the hay bacillus and those adapted to H_2 and CO_2 would grow better at partial tension than under aerobic conditions. As shown by previous observers, certain strains of the gonococcus and meningococcus grow best at partial tension when first isolated from the body; and these expts. on adaptation emphasize the importance of including the partial tension method of cultivation in the routine isolation of parasitic bacteria. It is believed that the well recognized fact that bacteria encountered in nature are aerobic, partial tension, anaerobic, or facultative in their respiratory requirements, is an expression of their previous adaptation. JULIAN H. LEWIS

Hemotoxin production by the streptococcus in relation to its metabolism. MARJORIA W. COOK, VIRGINIA MIX AND ETHEL O. CULVYHOUSE. Univ. Cal., *J. Infectious Diseases* **28**, 93–121(1921).—This work was done on the hemotoxic and other metabolic properties of a single strain of human *Streptococcus pyogenes* (Holman) grown under 2 conditions: (1) artificial medium since isolation (lab. strain); (2) the same passed repeatedly through the pleura of rabbits (pleura strain). Conclusions: There is a distinct difference in the hemotoxic properties of the laboratory and passage strains. This difference is not due to differences in the rate of multiplication alone. The inhibition of hemotoxin production in the laboratory strain as contrasted with the hemotoxic activity of the passage strain cannot be ascribed to a greater production by the former. Nor can it be ascribed to a greater acidity production by the former. Nor can it be ascribed to a greater protein-sparing action as evidenced by a greater utilization of glucose. The types of protein metabolism of the 2 strains are not sufficiently dissimilar to serve as an index to differences in hemotoxin production. The production of hemotoxin by the laboratory strain in a glucose serum culture, as contrasted by lack of hemotoxin production in a glucose culture, cannot be ascribed to any differences in metabolism which were measured. The only factor that can be said definitely to favor hemotoxin production is increased vitality of the organism. A summary of the entire study indicates only that hemotoxin production is due to, and controlled by, conditions that influence growth. JULIAN H. LEWIS

Differentiation between various strains of meningococci by means of the agglutina-

tion and the absorption of the agglutinins tests. C. T. BUTTERFIELD AND M. H. NEILL. U. S. Pub. Health Serv., Hyg. Lab., *Bull.* **124**, 9–42(1920).—A study was made of 191 strains of meningococci from various parts of the U. S. Classification of strains according to their geographic distribution is not possible. When the agglutination test with type serums prepd. from Gordon's types was applied to the Hyg. Lab. strains, 90% of them were classified without further work. If the meningococcus suspension agglutinates in a titer of 1:100 or higher, with only one of the type serums, provided the homologous coccus agglutinates in over 1:400, it can, in 100% of the cases, be classified at once without resorting to the absorption test. If a meningococcus suspension agglutinates with 2 or more type serums in equal titer, it can, in 100% of the cases, be classified by the absorption test. If a suspension agglutinates with 2 or more type serums in unequal titer, the highest titer probably indicates the type. This was true in 77% of the cases tried. In the monovalent serums tried, the complement fixation bodies have the same specificity as the agglutinins, the complement fixation titer being as a rule somewhat higher than the agglutination titer. During the course of a year's time the apparent changing of certain strains of meningococci from one type to another has been observed. A graphic method of selecting representative strains is presented.

JULIAN H. LEWIS

The fermentation reactions and pigment production of certain meningococci. CLARA E. TAFT. U. S. Pub. Health Serv., Hyg. Lab., *Bull.* **124**, 90–92(1920).—All the cultures produce acid in dextrose and maltose serum broth. All of them except 5 strains have no appreciable effect on saccharose broth or produce alkali in it. Sixty-four of the Hyg. Lab. stock strains of meningococci were tested for pigment production. Forty-eight produced the standard color called cream buff, 16 matched the color called cream.

JULIAN H. LEWIS

Studies on Azotobacter chroöcoccum Beij. AUGUSTO BONAZZI. *J. Bact.* **6**, 331–69(1921).—When this organism is grown in synthetic solns. its C relations vary with the age of the culture, and are closely connected with the N relations. The function of N fixation is not an important one, although it is present. JOHN T. MYERS

Solid culture media with a wide range of hydrogen- or hydroxyl-ion concentration. FREDERICK A. WOLF AND IVAN V. SCHUNK. *J. Bact.* **6**, 325–30(1921).—Agar or gelatin media if cooled to about 60° before being made acid or alk. will jellify at limits far beyond those tolerated by microörganisms. JOHN T. MYERS

Optimum hydrogen-ion concentration for the development of certain microörganisms. K. G. DERNBY. Pasteur Inst. *Ann. Inst. Pasteur* **35**, 277–90(1921).—The following values were found for a sugar-free bouillon, the first pair of figures representing the limits of growth, the other, the optimum concn.: *B. diphtheriae* 6.0–8.3, 7.3–7.6, *B. tuberculosis* (horse) 6.0–7.6, 6.8–7.2, *B. typhosus* 6.2–7.6, 6.8–7.2, *B. coli communis* 4.4–7.8, 6.0–7.0, *B. paratyphosus* A 4.5–7.8, 6.4–7.0, *B. paratyphosus* B 4.5–8.0, 6.4–7.2, *B. suipestifer* 5.0–8.2, 7.0–7.6, *B. pyocyaneus* 5.6–8.0, 6.6–7.0, *B. proteus vulgaris* 4.4–8.4, 6.0–7.0, *B. prodigiosus* 5.0–8.0, 6.0–7.0, *Sp. cholerae* 6.4–7.9, 7.0–7.4, *cinnabarens* 5.0–7.8, 6.0–7.0, pneumococcus, 7.0–8.3, 7.8, *Streptococcus liquefaciens* 5.5–8.0, 6.2–7.0. staphylococcus 5.6–8.1, 7.2–7.6, gonococcus 6.0–8.3, 7.3, *B. subtilis* 4.5–8.5, 6.0–7.5, *B. anthracis* 6.0–8.5, 7.0–7.4, *B. anthracoides*, 6.0–7.8, 6.8–7.2, coccobacillus of Pfeiffer 6.2–7.6, 7.0, *B. pestis* 5.6–7.5, 6.5–7.1, *B. sporogenes*, *B. histlyticus*, *B. canadiensis*, *B. putrificiens*, and *B. perfringens* all 5.8–8.5, 6.0–7.6, *B. tetani* 5.5–8.3, 7.0–7.6.

E. R. LONG

The bacteria of milk. A lactic ferment very frequent in milk, Streptococcus lacticus mucosus. H. VIOLLE. *Ann. inst. Pasteur* **35**, 218–29(1921).—An organism is found in many milks which forms lactic acid from sugars, produces a mucoid substance, and grows in chains. It is Gram-positive, and grows only in media contg. sugar. $NaNO_3$

greatly aids growth. The optimum temp. for growth is 30°. A half hr. at 60° kills. It does not attack the casein of milk. It utilizes amino acids. Indole is not formed. It attacks lactose, saccharose and maltose, but does not attack pentoses or hexoses, starch, inulin, dextrins, glycerol, sorbitol or mannitol. Reducing and oxidizing enzymes are not formed. The organism is not attacked by bile. It is non-pathogenic.

E. R. LONG

Studies on the Azotobacter. E. KAYSER. *Compt. rend.* **172**, 939–40(1921); cf. *C. A.* **15**, 1738.—A 2.5% soln. of mannitol contg. the usual salts was divided among 6 conical flasks and sterilized; 3 flasks were inoculated with cultures grown under yellow light and 3 with cultures grown under blue light. Two of each set were placed in a thermostat at 27° and one of each was left at room temp. After 13 days one of each set placed in the thermostat was analyzed for fixed N and for mannitol destroyed; after 26 days similar detns. were made in the contents of the 4 remaining flasks. The amt. of N fixed per g. of mannitol destroyed was generally larger from the yellow- than from the blue-light cultures. Less than 0.5 as much N was fixed at 8–10° as at 27°, but more than twice the amt. of N per g. of mannitol destroyed was fixed at the lower temp., that is at ordinary temp. the bacterium assimilates N more slowly but utilizes its food more efficiently. L. W. RIGGS

Phenomena of anaphylaxis in bacteria. CHARLES RICHET, MISS E. BACHRACH AND HENRY CARDOT. *Compt. rend.* **172**, 512–4(1921).—Lactic acid bacteria were cultivated during several months in nutritive solns. containing 0.0, 0.01, 0.1, and 1.0 g. $TlNO_3$ per liter. If the diverse varieties thus produced are shown on a medium containing 2 g. per liter of $TlNO_3$, it was observed after 24 to 48 hrs. that cultures from the first culture containing 0.0 $TlNO_3$ (control) had an acidity called 100; from the 0.01 culture, acidity, 26; 0.1 culture 80; and from the 1.0 culture 154. These results are discussed from the point of view of anaphylactic action. It is suggested that the phenomena of anaphylaxis is common to all living cells including bacteria. L. W. R.

Note upon the extraction of acids from cultures. R. GREIG-SMITH. *Proc. Linnean Soc. N. S. Wales* **46**, 154–156(1921).—In testing the formation of acid by a film yeast, succinic acid was obtained as the only fixed acid, but during its sepn. several interesting observations were made. It was found that the extn. of fixed acids from bacterial or yeast cultures is of the nature of a monomol. reaction and should be continued until no more acid is extd. The prepn. of salts such as those of Ba by neutralizing the extd. acids until a pink color is obtained in the presence of phenolphthalein may be faulty, as the reaction is much slower than is generally supposed. F. W. T.

The high-temperature organism of fermented tanbark. I. R. GREIG-SMITH. *Proc. Linnean Soc. N. S. Wales* **46**, 76–98(1921).—In the manuf. of white lead, plates of metallic lead are generally corroded by the old Dutch fermentation process. Fermentation stacks are built up out of layers of tanbark with the lead contained in pots between successive layers of bark. The author has investigated the fermenting organisms which are involved in this fermentation and their temp. relations. The fermentation occupies about 4 mo. and is about 60–80% efficient. The temp. starts at about 140° F., rises during the 2nd mo. to 180–190° F. and falls to 140° F. when the stacks are drawn. A sample of bark was taken from a stack at the top tier when it was in active fermentation. Microscopic examn. showed thread forms and stout rods. Some difficulties in culturing had to be overcome before the author was able to isolate a high-temp. organism responsible for the fermentation. The organism finally isolated was a stout rod of 3–4.5 μ in length and 0.7 μ in width. Terminal spores were formed which were oval at first and rounded later on. The organism is Gram-negative at 60° and positive at 37°. The optimum temp. of cultivation is 60°. It is capable of fermenting the spent wattle-bark of tanneries after the bark has been treated or tempered. The

tempering is undoubtedly a fermentation and in it a temp. of 40–50° is attained. In the stack there is probably a slow and prolonged evolution of CO_2 due mainly to bacterial action. F. W. T.

D—BOTANY

CARL L. ALSBERG

Protein content of maize. E. M. EAST AND D. F. JONES. Harvard Univ. *J. Genetics* **5**, 543–610(1920).—Breeding expts. show that a high protein content can be obtained only at the expense of a high production per unit of area. H. V. ATKINSON

The inheritance of green and yellow pigments in maize seedlings. E. W. LINDSTROM. Univ. Wisconsin. *J. Genetics* **6**, 91–110(1921).—The inheritance of 3 factors white, green, and yellow, and their respective allelomorphs, which govern the formation of green and yellow pigments in maize seedlings, is shown to be typically Mendelian. H. V. ATKINSON

The relation of protein content to variety types in American wheat. H. F. ROBERTS. *J. Agr. Sci.* **10**, 121–34(1920).—From a critical review of the American literature on this subject R. draws the following conclusions: No wheat variety possesses all of the desirable characteristics. In the case of winter wheat a high protein content is favored by a short, comparatively dry growing season, especially in the spring. The most important factor in detg. the starch-protein ratio is water supply. Regional types of wheat range from 9.16% protein to 13.89% protein. While with respect to regions of the country variation in protein content ranges from 11.35% in the Atlantic and Gulf States to 12.74% in the Western States, and 9.73% in the Pacific Coast States. Wheats which were grown in Maine and contained 12.2% protein showed 14.52% when raised in Minnesota. Differences in protein content due to variety were as follows: bread wheats 13.44 to 13.68%; Russian durums 14.2 to 15.19%; and Mediterranean durums 14.51 to 16.14%. Within the bread wheats varietal differences were noted. "The variation in protein content is measured by the error of mean square, or 'standard deviation.' It appears that, computing the data from California and Utah, the wheat varieties most widely grown in those States are the ones that turn out, according to the writer's computation, to have the widest variability in respect to their protein content, *i. e.*, which have the highest standard deviation." R. B. DEEMER

Respiration of dormant seeds. HOPE SHERMAN. *Botan. Gaz.* **72**, 1–30(1921).—The seeds selected were *Amaranthus retroflexus, Chenupodium album, Crataegus* (*C. coccinea* chiefly) and the common drupaceous Rosaceae. Catalase activity was measured by the vol. of O_2 liberated from H_2O_2 (the Oakland Chem. Company's dioxogen) by a given wt. of seeds. The app. was that described by Appleman (*Botan. Gaz.* **52**, 182 (1911)). The respiration detns. were made by means of a respirometer designed by Crocker [Paper by Crocker to be published. See S.'s paper for details. Abstr.]. Catalase activity increases in *Crataegus* under after-ripening and germinating conditions (10°) up to the 42nd day. Respiration reaches a max. intensity from the 6th to the 8th day. In *Amaranthus* both catalase activity and respiration are relatively stable. The respiratory quotient (CO_2/O_2) and the respiratory intensity (which corresponds to the mg. CO_2 eliminated per hr. per g. of imbibed seeds) vary markedly for different seeds. BENJAMIN HARROW

Water hyacinth. ROBERT S. FINLOW. *Rept. Agr. Dept. Bengal* **1918-19**, 120 pp.—The plant was burned and the ash extd. with H_2O. The *salts* obtained on evapn. consist of approx. 90% KCl and 5% K_2SO_4. Good ash contains 15% H_2O and over. Several tons of salts were obtained; the process may be of commerical value. RUSSELL M. JONES

Some errors concerning the localization of chemical compounds in the seed of wheat and rice and concerning the so-called aleurone. ICILIO GUARESCHI. *Ann.*

accad. agr. Torino **61**, 3-31(1918).—True gluten is found only in the seed of wheat (*Triticum*) and rye. The endosperm of wheat, rice and other cereals contains not only starch but also protein matter which may or may not be gluten. Gluten, whether it is preëxistent in the endosperm or is formed by the action of H_2O, occurs together with starch in the endosperm and not in the so-called aleuronic layer nor in the more external layers. The quantity of gluten increases from the center towards the periphery of the endosperm. Hofmann's violet decolorized by H_2SO_3 (1 g. $(EtNHC_6H_4)_3CH$ in 500 cc. H_2O to which are added 6–8 g. $NaHSO_3$ and 9–10 cc. HCl of sp. gr. 1.19) gives with proteins a beautiful blue or violet-blue, which can be used to detect the protein substances in flours. Though gluten can be easily sepd. from the starch of wheat it is difficult to sep. the protein matter from the starch of rice. Rice contains glutenin or glutencasein, some glutinfibrin, some edestin or phytovitellin but no gliadin, which characterizes true gluten. Rye and wheat contain some gliadin, some glutenin and some conglutin (which appears identical with edestin) and furnish a true gluten. It is erroneous to say that aleurone is synonymous with gluten. The name aleurone should be abolished.

ALBERT R. MERZ

The course of the absorption of ions by plants. E. PANTANELLI. *Bull. orto botan. Univ. Napoli* **6**, 1-37(1921); cf. *C. A.* **14**, 1842.—The respective absorptions of the 2 ions of various salts by the roots of the higher plants (*Lupinus albus, Vicia Faba* and onions), by marine algae (*Valonia utricularis*) and by yeast cells (*Saccharomyces*) were detd. by analyses of the solns. of the salts after immersion of the plant organ in it for different intervals of time, the original salt soln. being of known strength. The velocity of absorption is very different for different ions and also for the same ion it varies according to the external and internal conditions of the plant. The penetration of a given ion is much more rapid into unicellular organs or those rich in plasm than into pluricellular organs or those poor in plasm. The time-absorption curves vary greatly for the different ions, for the different plants and for the 2 ions of each salt. Absorption of the cation and the anion are completely independent, both as regards velocity and quantity. In expts. of long duration the curves for the two ions may touch because the fixation of 1 of them has already stopped or its expulsion has begun while the other continues to penetrate. In cases of more or less rapid absorption of a single ion the other may be found entirely outside, not having penetrated the cell at all, this indicating the separate absorption of the ions. No fact favors the concept that the entire molecule of the salt enters the cell, one of the ions being then expelled and the other fixed by double decompn. or combination in the cell. If the contact is sufficiently long those ions which at first remain without slowly penetrate. While the easily penetrating ions can in a few moments reach a concn. within the cell greater than that without, those which penetrate with difficulty do not for the most part attain diffusion equil. except where in toxic concns. they totally alter the absorbent properties of the protoplasm. The absorption is not continuous (progressive) for the rapidly penetrating ions since a partial excretion of the same ion follows its strong and rapid absorption, then a new absorption, often less than the first, then excretion, etc., the process assuming an oscillating course recalling that of a damped pendulum. These processes take place completely independently of the absence of equil. in concns. or diffusion forces because there can be not only an accumulation of ions in the cell as a result of rapid penetration but also active excretion from the cell into the soln. in which the given ion is in greater concn. than in the cell.

ALBERT R. MERZ

The physico-chemical properties of plant liquids. FR. NICOLOSI RONCATI AND G. QUAGLIARIELLO. *Bull. orto botan. Univ. Napoli* **6**, 257-9(1921).—The liquids examd. were sap from the vernal vine shoots of *Vitis vinifera* and *Vitis riparia*, sap from the trunk of *Virgilia grandis* and latex from *Euphorbia helioscopia, Euphorbia cyparissias*

and *Ficus carica*. The results show that the sap of *Vitis vinifera* is a very dil. soln. of salts (sp. gr. 1.000–1.002) with a viscosity practically equal to that of H_2O. The f. p. was lowered 0.020–0.041° indicating a concn. of salts, calcd. as NaCl, of 0.005 g. per l. The exceedingly low viscosity and absence of turbidity on addition of alc. show the almost if not complete absence of proteids. The H-ion concn. (10×10^{-7} to 20×10^{-7}) shows the salts to be at least in part acid salts. Variations in salt content of samples from the same *Vitis vinifera* taken from March to May (during flowering) were so small and so irregular as to be attributed to difference in samples only. *Vitis riparia* has a sap (sp. gr. 1.004–1.005) which gives higher elec. cond. values and a more acid reaction indicating a greater concn. of acid salts (H-ion concn. 35×10^{-7} to 42×10^{-7}). The very low viscosity (1.02) shows absence of proteins. Results for other samples were

	Sp. gr.	Viscosity at 25°.	Elec. cond. mhos at 18°.	H-ion concn.	Lowering of f. p.	
Virgilia grandis	1.014	1.074	0.00138	0.93×10^{-7}	0.243°	Sap.
Euphorbia helioscopia	1.053	2.90	0.0163	$68\times10^{-}$	——	Latex
Euphorbia cyparissias	1.047	2.38	0.0166	63×10^{-7}	——	"
Ficus carica	1.064	——	0.0147	90×10^{-7}	——	"

ALBERT R. MERZ

A plant oxidase acting on phlorhizin. GIOVANNI LEONCINI. *Staz. sper. agrar. ital.* 53, 138–45(1920).—An aq. soln. of phlorhizin kept at 15–20° assumes on the addition of wheat seed or wheat bran a beautiful straw-yellow to golden yellow color, which disappears only after putrefaction of the seed or the development of molds. This is due to a true oxidase and not peroxidase. It has not been identified as any of those oxidases which have been individualized by their action on definite chem. compds. Whether the oxidase directly oxidizes the phlorhizin or acts on phloretin produced by the action of a hydrolyzing enzyme remains to be detd. ALBERT R. MERZ

Chemical constituents of pine leaves. II. ASTRID CLEVE v. EULER. *Tekn. Tids. Kem. Berg.* 51, 35–8, 47–52(1921).—The former article concerned itself with the substances isolated from the powdered pine leaves by soln. in Et alc. and Et_2O, *i. e.* "crude fat." In the present paper there is presented a discussion of the parts which contaminated the crude fat but arenot sol. in Et_2O. It constituted about $^1/_3$ of the fat ext. This material is more conveniently extd. by means of 93% MeOH. Obtained in this way it accounts for fully 10% of the sample. It is designated as a "crude gum." This crude gum readily changes into an insol. substance. This change is facilitated by the presence of acids. The Et_2O-washed material crumbled into a powder. It dissolved in 5% NaOH. When recovered from this soln. by acidulating, its analysis gave less H_2O. The alk. soln. of the gum showed marked changes when treated with CO_2 or was contaminated by the CO_2 of the air. The crude fat plus crude gum material was treated with 5% NaOH. From the mixt. the fat could be sepd. mechanically. Fractions of the crude gum were then obtained by acidulating to just under the neutral point, to neutral, and to acid reaction. The first fraction was ten times as large as the second. The third was relatively very small. A 4th fraction was obtained by boiling off the Et_2O. The last two were very tannin-like. The 1st gave analysis and tests conforming to coniferyl alc. The second corresponded to dihydroxyhydrocinnamic alc. The whole crude gum was tannin-like in that it pptd. glue. Many analyses are given of fractions obtained in several ways and Pb ppts. Several columns are given to theoretical discussion. The crude gum is considered as consisting of intermediates in the plant synthesis of tannins. It stands between the lignin and tannin. It is not easy to differ-

entiate between the gum and tannin. The line of demarcation is placed at the point where pptn. ceases when water is added to the MeOH ext. in alc. soln. A. R. R.

The hydrocyanic acid content of Phaseolus lunatus. H. LÜHRIG. *Pharm. Zentralhalle* **62**, 95–97(1921); cf. *C. A.* **14**, 2038.—After soaking 50 g. beans, *Phaseolus lunatus*, with 200 cc. 1% HOAc for 24 hrs. the HCN content was detd. by distg. into a $AgNO_3$ soln. The pptd. AgCN was put into soln. by warming with NH_4OH for a short time, filtered and HNO_3 added in slight excess to reppt. the AgCN, and the amt. of Ag detd. from the wt. of the ppt. Because of the turbidity and color the distillate cannot be titrated directly with $AgNO_3$. The HCN content of 20 samples tested varied from 2.3 to 37.7 mg. per 100 g. The fermentation of the neutralized residue left after steam distg. by the addition of sour milk did not materially increase the HCN content. Beans cooked $3^1/_2$–4 hrs. in an open vessel with 2 changes of water showed an HCN content of 0.4 to 0.96 mg. per 100 g. H. A. SHONLE

Plant physiology. H. J. WEBBER. Calif. Agr. Expt. Sta., *Ann. Rept.* **1920**, 65–6.—*Growth and sap concn.* Rapidly growing trees have more dil. sap than more slowly growing trees of the same variety. Higher sap concn. and slower growth appear to be associated with the production of fruit buds. *The role of variability in detg. the efficiency of plant culture solns.* A comparison of Shive's nutrient solns. resulted in only slight differences in growth in the different solns. *Effect of N applications at different periods of growth of cereals.* The max. yield of spring wheat for the given application of N was obtained when it was added between a period of 4 to 9 weeks after planting. The different N salts are equally effective when applied at different periods of growth of the plants. *Do plants produce growth inhibiting and growth stimulating substances?* The results obtained would indicate that growth inhibiting and growth stimulating substances may be produced by plants and can affect the plant's growth. J. J. SKINNER

The chemistry of plant and food products. H. J. WEBBER. Calif. Agr. Expt. Sta., *Ann. Rept.* 1920, 69–71.—In redwood, a typical conifer, about half of the furfural yield is due to unhydrolyzable material in the cellulose residue, a small amt. to lignin and the remainder to easily hydrolyzable pentosan. J. J. SKINNER

Constituents of Pelretia wrightii Yendo. KINSUKE KONDO. *J. Chem. Soc.* (Japan) **42**, 259–72(1921).—"Yezo-ishige," *Pelretia wrightii* Yendo, is a seaweed. Although its use is not established in Japan, the related species in the Continent are used industrially for fertilizer, feed, and AcOH fermentation. K. discovered that this is a good source of fucose, which was necessary for the estn. of pentosans and methylpentosans. The air-dried substance contained H_2O 4.74, ash 29.54, protein 7.47, fat 1.71, crude fiber, 2.48, sol. non-nitrogenous substance 54.05, pentosans 6.40, methylpentosans 2.04, fibrin, galactan and mannitol 1.48%. One kg. of the weed hydrolyzed with 4% H_2SO_4 (5 l.) and treated with phosphomolybdic acid, $Ca(OH)_2$, and 90% alc. gave 37 g. of sirup which gives positive reaction with Molisch, Fehling, is levorotatory and shows the characteristic pentose spectrum after phloroglucinol-HCl treatment, both furfurol and methylfurfurol being obtained by HCl distn. No mucic acid nor gluconic acid crystals were found on oxidation of concd. HNO_3. Seliwanoff and Pinoff tests are negative, no Cd crystals after Betrand method. These tests show presence of pentose and methylpentose, the former being arabinose and the latter fucose. S. T.

The influence of the nature of the soil and fertilization on the content of nitrogen and ash constituents in our crops. J. G. MASCHHAUPT. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* No. **25**, 115–29(1921); cf. *C. A.* **13**, 1353, 2103, 2953.—In previous years the influence of nitrogenous fertilizers ($NaNO_3$, $(NH_4)_2SO_4$, KNO_3) on the compn. of crops had been studied, so in 1918 the influence of a fertilizer contg. potash and phosphoric acid was studied on 5 different soils (moor-, marsh-, peat-, loam-, and

clay-soils). The first series received no potash or phosphoric acid, only N, the second received a complete fertilizer (N+P+K), the third series N+K and the fourth series a complete fertilizer with twice the amt. of potash (N+P+2K); the details are given in a table on page 117. The yield of grain (from the wheat sown) for the different fertilizers on the different soils is given in table 86 while the yield in straw and chaff is given in table 87. Table 88 gives the total yield of grain and of straw + chaff on the different plots, reckoning the yield on clay as 100. The influence of soil on wt. per hectoliter is shown in table 89 where it appeares that marshy soil ("broekgrond") gives a wheat grain with the highest and loam soil ("zavelgrond") the lowest wt. per hl. Further it was noticed that marshy soil gave the most glassy and loam soil the most mealy grain, which is undoubtedly related to the high N content of the wheat grains of the marshy soil and the low N content of the grains of the loam soil. Table 90 gives the av. % of N and of the various ash constituents (calcd. on a dry basis) in the wheat grain, straw and chaff obtained from each field. The differences in the SiO_2 content are remarkably great (see table 91 where the SiO_2 contents of the different straws grown on different soils are compared). In table 92 the content of the grain and the straw is once more given in equivalence, N being calcd. as 100. From these tables can be seen the influence of soil on the compn. of the crops. The influence of fertilizer on the compn. of wheat is very small; even the fertilizer with double the quantity of K seems to have very slight influence on the K content. The av. compn. of the 5 lots is given in table 93. It must, however, be borne in mind that the exptl. plots were in a good state of fertilization as regards K and P_2O_5 so that bigger differences in compn. may become apparent if the 1918 method of fertilization is kept up for a few years. Table 94 gives the quantities in kg. of N and ash constituents removed from the ground per ha. by the wheat from the 5 soils fertilized with N+P+K and in comparison is given the quantities per ha. of N, P_2O_5 and K_2O used as fertilizers. Table 96 gives the compn. of 2 samples of winter wheat grown on 2 samples of dollard clay. Furthermore one finds for comparison the results from table 90 for loam soil and clay and finally an analysis of summer barley, winter barley and peas grown on the same kind of clay in different observation fields and of some yellow fodder beet grown on the dollard clay at this expt. station. The summer and winter barleys and the fodder beets are compared with crops of previous years. The fact that the Ca content of the crops does not at all depend on the richness in Ca of the soil on which the crops are grown is shown beautifully by the results obtained with oats (see table 98) which were grown in a soil (aphrite) contg. 73% $CaCO_3$, yet as is seen in table 100 if the compn. is expressed in equivalence with N as 100 the Ca content is very low, especially as compared with that of crops grown on old clay. Other remarkable facts seen in this table are the exceptionally high N content; the straw contained 2.30% N of which 0.7% was present as nitrate and 0.18% as NH_4NO_3. VINCENT VERMOOTEN

The composition of our crops in successive periods of growth. J. G. MASCHHAUPT. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* No. 25, 131–8(1921).—In order to det. at what period of growth a plant chiefly takes up N, P_2O_5, etc., and whether the N and ash constituents which are present in the ripe crops are also present at any period of growth; 6 crops of potatoes were planted between June 4th and Aug. 29th. The foliage and tubers were analyzed; the roots were not analyzed because M. found it practically impossible to isolate the roots and because in any case one does not get reliable analytical material from them. Table I shows the percentage compn. of the N and of the various ash constituents in both the foliage and the tubers, at different periods of growth. Table 2 shows the amts. of N and of ash constituents in 9 plants while in Table 3 these amts. are expressed in percentages of the max. amts. present at any time of growth; Table 4 furthermore gives an insight into the formation of the dry matter

of the tubers and of the starch formation. From this it becomes apparent that in ripe potatoes there are larger amts. of N and ash constituents than at any earlier period; thus there is no migration back into the soil. These results coincide with those of Wilfarth, Romer, and Wimmer. Further in Table 5 M. gives sep. analyses of the roots and of the stalk and leaf. M. mentions an expt. on the possibility of extg. the ash constituents from fresh potato foliage by means of water. Table 6 shows that appreciable amts. of ash constituents are given up after 7 hours immersion in water; the possibility thus remains that considerable amts. of salts may be washed out of the leaves in very rainy seasons. VINCENT VERMOOTEN

Photocatalysis. I. The synthesis of formaldehyde and carbohydrates from carbon dioxide and water (BALY, *et al.*) **10.** Lichen products. III. Determination of the constitution of divarin (SONN) **10.**

F—NUTRITION

PHILIP B. HAWK

NORMAL

Calcium equilibrium in the body. OSCAR LOEW. *Chem.-Ztg.* **45**, 373–4(1921).—This is a brief review of the present knowledge of Ca metabolism. Methods of detg. the Ca balance are discussed and the effects of various pathol. conditions mentioned. The daily elimination of CaO amounts to about 1.0 g. of CaO, of which 0.2–0.3 g. is through the urine. An increase of the amt. in the urine indicates acidosis. H. points out that the usual assumption that the ordinary food contains sufficient CaO for human needs is not necessarily correct; the quality of the food must be considered. Cf. *C. A.* **15**, 2471. A. L. BARKER

New theories of nutrition. ANDRE LEROY. *Bull. soc. hyg.* **8**, 67–86(1920).—A review of the more recent work along this line, including that on the role of the amino acids as well as that on the problem of the vitamines. A. L. BARKER

Effect of ration on the development of pigs. C. O. SWANSON. Kansas Agr. Expt. Station. *J. Agr. Research* **21**, No. 5, 279–341(1921).—*I. Chem. compn. of pigs as influenced by the character of the ration.* The plan was to feed one lot of 3 growing pigs on corn alone, another lot on corn and ash and other lots on corn supplemented with feeds calcd. to supply either the protein or ash deficiency in corn or both such deficiencies. The following supplementary feeds were used, *viz.*, com. bone ash, synthetic bone ash (Mendel's formula), black blood albumin contg. 80.75% protein and 3.61% ash, milk protein, milk casein, milk albumin, protein-free skim milk contg. 0.68% ash, 0.34% nitrogenous compds. and 5.9 % sugar, and corn germ contg. 16.5% protein, 5.64% ash and 19.13% ether ext. Com. corn starch was used. The ash-free blood protein contained when dry 95.06% protein, 1.09% ash, 0.0126% Ca and 0.082% P. The amts. of the several chem. constituents in the various feeds consumed by the pigs are tabulated. One or 2 representative pigs were slaughtered and analyzed at the beginning and end of the expt. The following data were obtained: live wt., wt. of blood, wt. of dressed carcass, wt. of several internal organs, wt. of stomach, intestines, and bladder before and after removing contents, wt. of fatty tissues, lean tissue, skin and bones, and chem. compn. of the different portions into which the animals were divided. The % of H_2O, ash, protein and ether ext. as well as the age and empty wts. of the slaughtered pigs are recorded. Pigs fed rations decidedly deficient in ash or protein had a very restricted growth; the compn. of their bodies showed wide variation in different animals and generally a low fat and a high H_2O content. Pigs fed a partially deficient diet but one sufficient to produce a restricted growth had a high fat content. Pigs fed a ration balanced in respect to the protein and ash contents showed nearly equal H_2O and fat contents with a tendency for the latter to be a little lower. In pigs weighing less than 225 lbs.

whose ration was partially restricted the fat content was higher than the H_2O content. A pig, weighing above 225 lbs. and fed a ration sufficient to produce large and rapid growth, showed the % of fat increases as the wt. increases and the % of H_2O decreases. The prolonged feeding of a deficient diet produces the same result provided the pig attains large size. The % of protein and of ash appear to decrease as the pigs increase in size, owing to large increases in % of fat. A large amt. of protein or ash will not produce a pig with a high protein or ash content. There is a closer relation between a pig's size and its compn. than between the character of the ration and the pig's compn. *II. Character of ration in its effect on the development of lungs, heart, liver and kidneys.*—The wts. of these organs to the empty wt. of the animals is recorded. The wts. increase with the increase in wt. of protein. The variations are irregular and no sp. relation to the character of the diet is evident. A ration which contains the nutrients for the normal development of the pig will develop the internal organs in the same ratio. The relative smallness of the internal organs in some pigs of restricted growth is due to the development of fat. The relation of the wts. of the internal organs to the wts. of protein fed is tabulated. *III. Relation between the amt. of chem. constituents consumed during the feeding trials and the amt. stored.*—Pigs that had attained a certain development when fed on corn alone stored an av. of 1 lb. of protein per 7.5 lbs. of protein consumed and the sum of ash, fat and body protein stored was 1.1 lb. per lb. of protein consumed. When the corn was supplemented with a small amt. of milk protein ($^1/_8$ to $^1/_{10}$ of the total protein in the ration) the pigs stored 1 lb. of protein per 5.11 lbs. consumed and the sum of ash, fat and body protein stored was 1.46 lb. per lb. of protein consumed. When corn was supplemented with a medium amt. of protein from milk, the pigs stored 1 lb. of protein per 3.5 lbs. consumed and the sum of ash, fat and body protein stored was 1.41 lbs. per lb. of protein consumed. When corn was supplemented with a large amt. of milk protein (from $^1/_3$ to $^2/_3$ of the total protein of the ration) the pigs stored on an av. 1 lb. of protein per 6 lbs. consumed and the sum of the ash, fat and body protein stored, was less than 1.1 lbs. per lb. of protein consumed. Of the 24 pigs in these expts. 9 stored more than 1 lb. of fat per lb. of protein eaten and the majority of the pigs stored 0.8 lb. to 1.0 lb. of fat per lb. of protein consumed. The source of the protein did not have a distinct influence. Pigs whose sole source of protein was corn stored less therms on an av. in proportion to the thermal value of the feeds consumed than did the pigs to whose ration animal protein was added. From the standpoint of energy storage (1) the small amts. of milk protein used were as efficient as the larger amts.; (2) the feeding of corn alone is not efficient; (3) the addition of $^1/_{10}$ to $^1/_4$ of the protein from other sources is as efficient as when $^1/_2$ or more of the protein comes from other sources. *IV. Effect of prolonged feeding of corn alone, corn and ash, or corn and protein-free skim milk on the growth and development of pigs.*—The live wt., gain and total food consumption per 100 day periods are tabulated for the different rations. The wt. of nutrients and therms in the rations consumed, the protein stored and thermal value, the fat stored and thermal value, also the summary of lbs. of protein consumed and lbs. of protein stored, the therms in nutrients consumed and therms in nutrients stored, and ratios are tabulated. Two pigs, one on a ration of corn and ash and one on a ration of corn and protein-free skim milk when $3^1/_2$ months old, did not make satisfactory gains until they had been on this ration for 500 days. One other pig on a ration of corn alone when $4^1/_2$ months old made very slow gains for 300 days, more rapid gains the following 400 days and rapid gains the last 360 days of the test. When corn was the sole source of protein in the ration, the ratio of protein stored to protein consumed was 1 to 7. The two pigs, one fed corn and ash, the other fed corn and protein-free skim milk, stored 1 therm for 18.82 consumed during the first 400 days of the expt.; during the last 500 days they stored 1 therm for every 3.19 consumed. The pig fed corn alone stored 1 therm for 8.23 consumed during the first 600

days and during the last 400 days 1 therm for 2.93 consumed. Numerous graphs are given. F. C. Cook

Some fundamentals of stable ventilation. H. P. Armsby and M. Kriss. Penn. State College. *J. Agr. Research* **21**, 343-68(1921).—Data are presented for fasting katabolism of cattle, for the increment of heat production by cattle per lb. of dry matter consumed, for typical live wts. and rations, total heat produced by typical cows per head per day, heat given off by radiation and conduction and as latent heat of H_2O vapor per day per head by typical cows, H_2O vapor produced by typical cows per head per day and the amt. of CO_2 produced by cows per head per day. Similar data are tabulated for horses, swine and sheep. The air flow per head necessary to maintain 0.167% CO_2, *i. e.*, the av. figure for CO_2 in air coming from the lungs and in pure air, the av. temp. differences maintained by animals and the temp. of the stable compared with that of outside air also the max. rate of air flow possible if a temp. difference of 50° F. is to be maintained, are recorded. Certain technical details of the problem are presented. F. C. Cook

Meat production. J. A. Murray. *J. Agr. Sci.* **9**, 174-81(1919).—This article is a discussion of the problems of meat production, in which M. develops a mathematical formula for detg. the "condition" of the living animal. This condition is defined as the ratio of the amt. of fat to the amt. of non-fatty matter in the body of the living animal, and the term "fattening" as any alteration in this ratio. Such alteration may result from (*a*) increase, or (*b*) decrease in the amt. of fat; (*c*) increase, (*d*) decrease in the amt. of non-fatty matter. It appears that the verbal terms used by practical experts to describe condition can be interpreted approx. as follows: Very lean (body fat, expressed as %), less than 5; lean, 5 to 10; store 10 to 15; fair (good store), 15 to 20; half fat, 20 to 25; moderately fat, 25 to 30; fat 30 to 35; prime, 35 to 40; very fat, 40. A curve for basal katabolism is given. R. B. Deemer

Influence of the nervous system on the excretion of creatinine. A. A. Weinberg. Univ. of Groningen. *Biochem. J.* **15**, 306-11(1921).—Patients at the hospital were put on a diet free from creatine and creatinine for 6 days. The amts. of urine of the last 3 days of the expt. were used to det. the av. excretion of creatinine. The creatinine was detd. according to Folin's method as applied by Autenrieth and Müller (*C. A.* **5**, 3464). In comparison with normal patients, who were under external circumstances similar to those of the patients experimented on, an increased excretion of creatinine was found with patients suffering from nervous disorders. The disorders were of such a nature that the normal connections between muscles and brain were damaged, and further that the patients were preoccupied and diffusely conscious. In contradistinction to Pekelharing (*C. A.* **5**, 1458) an increased creatinine excretion was found also with lowered muscular tonus. Benjamin Harrow

Antiscorbutic and antiberiberi properties of certain sun-dried vegetables. J. A. Shorten and C. B. Ray. Medical Coll., Calcutta. *Biochem. J.* **15**, 274-85(1921).—The vegetables were dried at the Government Fruit Expt. Station, Quetta, India, as follows: "The vegetables having been cleaned and prepd. are placed in fresh water, or in certain cases in a steeping soln. The prepd. material is then transferred to a wire basket and either scalded or steamed for a few min. The contents of the wire basket are now emptied on to the drying trays and dried in the sun. The dried product is collected in sacks or open boxes in which it is allowed to remain for about a week, during which time it is examd. at intervals for signs of dampness. After about a week the dried product is ready to be compressed into bricks and packed in air-tight tins." The methods were those commonly employed by other investigators. Dried tomatoes, potatoes and cabbage retain much of their antiscorbutic values when fed as a daily ration of 5 g. dried product to guinea pigs weighing on an average 500 g.; this is not

true of carrots, brinjal, spinach, turnips and turnip-tops. Cooking before consumption diminishes the antiscorbutic values. Carrots, brinjal, spinach, cabbage, tomatoes and potatoes showed antineuritic properties. BENJAMIN HARROW

Benefits from feeding mineral supplements. E. B. FORBES. Ohio Agr. Expt. Sta., *Mo. Bull.* 5, 206–15(1920).—A general discussion of the effect of Ca and P in the matabolism of animals. J. J. SKINNER

ABNORMAL

Galactose metabolism in infancy and childhood. SELMA MEYER AND GEORG STERN. *Arch. Kinderheilk.* 68, 241–54(1920).—In 63 tests of the galactose excretion in infants and children following oral administration of 10–60 g., the following results were obtained: Age seemed to have no influence upon the excretion of galactose. The ability of young children to assimilate galactose is not great, but not much different from that of older individuals. With the ingestion of 20 g. the output is not over 0.5 g., with 40 g. not over 3.0 g. There is no relation between body wt. and amt. excreted. Pathologically increased excretion is always associated with disease of the digestive apparatus although the liver cannot always be directly implicated. In most cases there was injury to the liver leading to functional disturbance which was responsible for the diminished tolerance. No direct influence upon galactose tolerance could be demonstrated in the acute exanthemata or in nervous diseases. E. B. FINK

The pathology of calcium metabolism. HANS EPPINGER AND EGON V. ULLMANN. Vienna. *Wiener Arch. inn. Med.* I, 639–49(1920).—The administration of 30 g. $NaHCO_3$ to two normal persons caused no change in the excretion of Ca and Mg. In two cases of tetany the Ca excretion increased 20 and 26%. The Mg excretion in one case increased 72% and in the other decreased. In two cases of hunger osteoporosis the Ca excretion increased 86 and 116% and the Mg excretion 23 and 147%. Administration of $KHCO_3$ in one case of osteoporosis caused an increase of Ca excretion of 101, in Mg excretion of 300%. It is suggested that while the normal individual is in a state of Na, K, Ca, Mg balance, this balance is disturbed in hunger osteoporosis. The meager war diet, consisting mostly of vegetables, was not only deficient in calories but poor in Ca, while rich in K. HARRIET F. HOLMES

F—PHYSIOLOGY

ANDREW HUNTER

The internal secretions. J. STROHL. *Rev. gén. sci.* 32, 262–73(1921).—S. reviews the publications of a number of authors with criticisms and comments. The arguments bear particularly on the interrelation of the endocrine excretions and the development of sexual characteristics. Expts. reported were on insects, paramecia, frogs, tadpoles and also mammals, and include ablation, transplantation and feeding of glands, and the effects of arrest of secretions. S. concludes that if it is a question of chem. correlation, as is apparent, chem. methods must be used in the study and verification of the various phenomena. H. C. HAMILTON

Composition of the unsaponifiable matter of the ether extract of human feces. J. A. GARDNER. Univ. of London. *Biochem. J.* 15, 244–73(1921).—An inconclusive account pointing to the presence in the "unsaponifiable matter" of a substance belonging to the sterol or polyterpene group. BENJAMIN HARROW

Effect of exposure to low temperatures on some physiological, chemical and physical properties of amphibian muscle. D. L. FOSTER AND D. M. MOYLE. Biochem. Lab., Cambridge. *Biochem. J.* 15, 334–46(1921).—Expts. are described in which it is shown that a non-irritable condition in muscle can exist without accumulation of lactic acid, provided the muscle is kept in air or O. In N the loss of irritability is more rapid and lactic acid is formed. It is, therefore, necessary to look upon loss of

irritability as a sep. phenomenon from the rigor of fatigue and death. A solution which is isotonic to a normal muscle is hypertonic to the non-irritable muscle, and a soln. which is hypotonic to a normal muscle is less hypotonic to the non-irritable muscle. The loss of irritability is probably of "ionic" origin. BENJAMIN HARROW

G—PATHOLOGY

H. GIDEON WELLS

The physiology of cancer. I. Tumors and their inorganic chemistry. N. WATERMAN. *Arch. Néerland Physiol.* **5**, 305–27(1921).—Expts. confirming the work of Beebe on human tumors and that of Frisbie on animal tumors. There exists in tumors an antagonism between K and Ca in proportion to the rate of degenerative changes. **II. The oxygen consumption of tumors.** N. WATERMAN AND M. DIRKSEN. *Ibid* 328–45. Increased. H. V. ATKINSON

Histologic changes in the central nervous system in thyroid deficiency. R. ISENSCHMID. Frankfurt. *Frankfurter Z. Path.* **21**, 321–36(1918).—Extirpation of the thyroid in cats is followed in 2–4 mos. by changes in the nerve cells of the central nervous system characterized by more or less marked interference with their property to stain with basic aniline dyes. The nuclei showed only slight changes in a few cells. E. B. FINK

Interpretation of changes in the hypophysis associated with diabetes insipidus. F. V. HAUN. Budapest. *Frankfurter Z. Path.* **21**, 337–65(1918).—On the basis of his own observations and a review of the literature H. draws the following conclusions: Every case of diabetes insipidus depends upon a dysfunction of the hypophysis. Hypophyseal disturbances lead to diabetes insipidus when the posterior lobe is involved either by a tumor or inflammatory processes while the anterior lobe remains either intact or at least functional. As a result of the dysfunction of the hypophysis there is a disturbance in its correlative action upon the other endocrine organs resulting in either a lack of inhibition or direct hormone action on the part of the nervous system followed by a loss of the ability of the kidney to concentrate urine; polyuria results. The occurrence of diabetes insipidus is related to the function of the kidneys and heart as well as the hypophysis. The question is raised of the relation of hereditary insipidus to syphilitic involvement of the hypophysis. E. B. FINK

The anatomical diagnosis and histology of phosphorus poisoning. ELSIE PETRI. Berlin. *Frankfurter Z. Path.* **25**, 195–215(1921).—The liver in P poisoning cannot be distinguished from acute yellow atrophy. By the use of elective histochem. methods in 5 cases of P poisoning, lipoids were demonstrated in the liver, kidneys and stomach belonging to the group of phosphatids, as well as neutral fats and mixtures of neutral fats and lipoids. The presence of lipoids speaks against the assumption that the fat in the liver is entirely infiltrated fat. There must be in addition a fatty phanerosis. P belongs to the toxic substances of known and unknown origin which produce acute yellow atrophy, and the anatomical and clinical picture of P poisoning is not a separate entity but belongs to the large group associated with acute yellow atrophy of the liver. E. B. FINK

Classification of gases according to the pathology produced in the lung. ROMAN ADELHEIM. Riga. *Frankfurter Z. Path.* **25**, 261–76(1921).—Gases can be divided according to their pathological effect upon the respiratory epithelium into indifferent and active. The first are absorbed during the physiological activity of the lungs in the gaseous exchange and after absorption may be toxic or non-toxic (H and N), the resorptive action of the gases being similar to their ordinary pharmacologic action. E. B. FINK

Studies on the parathyroids with special reference to the acidophilia of the cells. HANS KOOPMANN. Hamburg. *Frankfurter Z. Path.* **25**, 342–72(1921).—The hypoth-

esis of Lundborg that paralysis agitans is due to parathyroid disturbance has no pathologic-anatomical foundation. The acidophilia of the parathyroid cells is morphologic evidence of the relation of these structures to the hypophysis and pancreas. The acidophilia of the parathyroid cells increases with age up the 8th decennium.

E. B. FINK

The significance of mast cells. M. STAEMMLER. *Frankfurter Z. Path.* **25**, 391–435(1921).—Mast cells are single-celled glandular organs of the connective tissues whose function is the production of the mucin required by the interfibrillar cement substance. E. B. FINK

The feces in alimentary disorders. ROBERT COOPER. Liverpool. *Lancet* **1921**, II, 9–11.—A discussion of the influence of diet, and the macroscopical, microscopical and chem. examination of feces. The absence of stercobilin indicates that bile is not entering the intestine. E. B. FINK

The toxicity of organ extracts and the neutralizing action of blood serum. TSUNEO SAKAMOTO. Tokio. *Z. Immunität.* **32**, 1–6(1921).—The lung yields the most toxic ext. of all organs. The toxicity of lung tissue exts. is destroyed by heating at 100° for 2 hrs. and at 38° for 10 hrs. The ext. retains its toxicity for only about 2 days when kept on ice. Toluene protects it from loss of toxicity. The toxicity is only slightly reduced by filtration through a Berkfeld filter, by shaking with kaolin or animal charcoal and is not at all affected by a soln. of egg white. The toxicity of organ exts. is completely neutralized by the addition of fresh normal serum, but serum inactivated at 56° loses its neutralizing properties. There is an individual variation among sera in their neutralizing ability. A time interval is also necessary, usually several hrs. in the incubator. Detoxication of exts. is most efficient with homologous serum. The action of homologous serum cannot be explained by adsorption. Exts. are able to take up hemolytic complement in the same way as organ cells. The detoxicating substance cannot be extd. by acetone, alc. or Et_2O, nor is it dialyzable. The carbohydrates are not concerned in the detoxicating action of serum. Leucocytes, *in vivo* or *in vitro*, are unable to detoxicate exts. There is a direct relationship between the hemolytic complement and detoxicating substance. The detoxicating substance can be separated into a globulin and albumin fraction by pptn. with HCl and CO_2. The liver does not detoxicate exts. In general, detoxicating substance and hemolytic complement run parallel but are not identical. This is taken as evidence of a multiplicity of complements. Immune bodies, but not the protective ferments of Abderhalden, are concerned in detoxication of exts. E. B. FINK

The influence of temperature upon the reactivity of syphilitic sera. EBERHARD SCHWAB. Hamburg. *Z. Immunität.* **32**, 87–112(1921).—Incubation at 37° is not the optimum for all syphilitic sera in the Wassermann reaction. E. B. FINK

The function of the spleen in agglutinin production. VIKTOR K. RUSS AND LEOPOLD KIRSCHNER. Vienna. *Z. Immunität.* **32**, 113–36(1921).—Splenectomy performed 10 days before the injection of agglutinogen results in the appearance of less agglutinin in the blood serum of rabbits as compared with normal controls. A second injection of agglutinogens into splenectomized rabbits is followed by the vigorous production of agglutinins which appear more rapidly than in non-splenectomized animals. These observations indicate that the spleen plays an important role in the production of agglutinins, but that in the absence of the spleen this function may be vicariously assumed in a quant. manner by other organs over a long period of time. Splenectomy in immunized animals results in a drop in agglutinin titer which cannot be accounted for on the basis of shock produced by operation. There is no noticeable increase in agglutinin titer following the production of fever in splenectomized rabbits by the injection of pyrogenic substances (deuteroalbumose, milk, killed staphylococci).

In non-splenectomized animals only intravenous injections of pyrogenic substances produce an increase in agglutinin titer. E. B. FINK

The role of albumins and globulins in the serodiagnosis of syphilis. FELKE. Rostock. *Z. Immunität.* **32**, 137–53(1921).—The albumin fractions of luetic sera are able to produce ppts. in the Sachs-Georgi reaction. This is a confirmation of the work of Mandelbaum, Gloor and Klinger. It was further shown that in the reaction between Wassermann ext. and active luetic serum the complement middle-piece, as well as the end-piece disappears. It is possible to obtain reactions with the separate albumin and globulin fractions which are albumin end-piece and globulin middle-piece reactions depending upon changes in the fractions derived from luetic serum under the influence of Wassermann exts. E. B. FINK

The mechanism of the antihemolytic action of quinine alkaloids. ALFRED SCHNABEL. Basel. *Z. Immunität.* **32**, 153–66(1921).—The action of quinine and optochin in immune hemolysis was studied. These alkaloids in concd. solns. possess the property of hemolyzing erythrocytes and in various concns. they definitely interfere with immune hemolysis. They have a peculiar action upon red blood cells in that they are at first taken up by them and then released. The antihemolytic action of these 2 alkaloids is due to their absorption; hemolysis occurs when the alkaloids are given up by the red cells. E. B. FINK

The Sachs-Georgi and Meinicke reactions. MARGARETE STERN. Breslau. *Z. Immunität.* **32**, 167–85(1921).—The Sachs-Georgi reaction agrees with the Wassermann reaction in 88% of cases. The S.-G. reaction is more sensitive than the Wassermann reaction in latent and treated lues while the reverse is true in lues I and II. In spinal fluids the two tests agree in 86% of cases. The S.-G. reaction is valuable as an adjunct to the W. reaction. Similar results were obtained with the Meinicke reaction. E. B. FINK

The Rieckenberg reaction. MARIE RICHTER. Jena. *Z. Immunität.* **32**, 186–94(1921).—The Rieckenberg reaction consists of a sp. clumping of blood platelets around trypanosomes in animals that have overcome a trypanosome infection. Expts. were performed to test out whether this reaction occurs in the ordinary generalized streptococcus and staphylococcus infections. Such a reaction would explain the occurrence of infectious thrombosis in these conditions. The results indicated, however, that in rabbits injected with strepto- or staphylococci there is no such reaction as the Rieckenberg reaction between blood platelets and the organisms. E. B. FINK

A study of high blood pressure in women from the endocrine point of view. J. GUTMAN. *N. Y. Med. J.* **114**, 31–5(1921).—Clinical observations lead to the opinion that when every other possible pathological factor has been excluded an essential hypertension in multiparous middle-age pituitotropic women is due to an increase in the blood-pressure-raising pituitary hormone produced by a greatly hypertrophied, hyperfunctioning hypophysis. The pituitary hormone is considered to be a normal factor in the maintenance of arterial hypertension. F. S. HAMMETT

The clinical value of basal metabolism determinations in diseases of the thyroid gland. HERMAN O. MOSENTHAL. *N. Y. Med. J.* **114**, 41–3(1921).—A report of two cases which strengthens the opinion of M. that basal metabolism detns. in thyroid disorders furnish the best measure by which to gage the effect of medication, X-ray or operation. F. S. HAMMETT

Basal metabolism and endocrine manifestations. A. S. BLUMGARTEN. *N. Y. Med. J.* **114**, 43–6(1921).—Since the basal metabolic level is raised in hyperthyroid and lowered in hypothyroid conditions, its detn. can be used as an aid in detg. the presence or absence of thyroid disturbance in various common diseases. F. S. HAMMETT

The origin of hemolytic icterus. PAUL KAZNELSON. Prague. *Wiener Arch.*

inn. Med. **1**, 563–574(1920).—The following findings in a case of hemolytic icterus indicate that the spleen plays an important role in the origin of hemolytic icterus. The fragility of the erythrocytes towards hypotonic salt solution was greater in blood from the splenic vein than in blood from a peripheral vein. The amt. of bilirubin in blood from the splenic vein was twice the amt. of that in blood from a vein of the abdominal wall. The removal of the spleen caused a marked improvement. A description is also given of a case of cholemia familiaris in which the blood contained eight times the normal amt. of bilirubin, but without the other findings characteristic of hemolytic icterus, representing a connecting link between bilirubinemia and true familial hemolytic icterus.

HARRIET F. HOLMES

Specificity of the antigen of Besredka. A. URBAIN AND B. FRIED. *Ann. inst. Pasteur* **35**, 294–9(1921).—The complement-fixing power of Besredka's antigen was tried in the presence of 1:20 emulsions of the bacterial bodies of a variety of organisms. Antituberculous horse serum, prepd. by repeated inoculation with tubercle bacilli, and serum from human tuberculous subjects, in contact with the antigen of Besredka, fixed alexin in high amt. The same sera behaved like normal sera in the presence of other antigens, including streptococcus, pneumococcus, *B. coli, B. typhosus, B. paratyphosus, B. mallei, B. anthracis and B. subtilis.* In three cases out of 20 a positive reaction was noted with the serum of tuberculous patients and diphtheria antigen. The sera of horses immunized against various bacteria did not give positive reactions when used with the tubercle bacillus antigen, except in the case of the antiserum to *B. diphtheriæ*, in which case a weak fixation occurred. The serum of typhoid fever, erysipelas and nephritis patients did not give positive complement fixation with the Besredka antigen.

E. R. LONG

The antigenic value of bacillary emulsions and of ethyl alcohol and methanol extracts of tubercle bacilli. L. NEGRE AND A. BOQUET. *Ann. inst. Pasteur* **35**, 300–14 (1921).—The authors consider the peptone B_2 antigen of Calmette and Massol (*Bull. inst. Pasteur* **1916**, 33) and the egg antigen of Besredka (*Ann. inst. Pasteur* **1914**, 428) the most active tubercle bacillus antigens, but point out that the former is obtained only by the use of a peptone rich in albumose, not always available, while the Besredka antigen keeps but a short time. Alc. antigens, such as the antigen described by Petroff, *C. A.* **11**, 1475, have been too little sensitive in the case of EtOH, or excessively so in the case of MeOH. The authors have modified the alc. extn. method of prepn. by preliminary treatment with acetone, previous investigations having apparently shown that the acetone removes a great number of lipoids unessential to the reaction, leaving the essential phosphatides. Their method is as follows: Tubercle bacilli grown 6 wks. on glycerol broth are sterilized at 120° for 1 hr., washed with water, dried in the oven, and left in contact with 100 vols. of acetone 24 hrs. The mass is then filtered off and treated with alc. in the same proportion 10–12 days at 38°. The mixt. is filtered and the clear ext. dild. 1:10 for use. Such an ext. deposits a light ppt. on cooling and gives an opalescence comparable to a 1:10,000 lecithin emulsion in water. Titration of antigens prepd. by this method showed that human and bovine tubercle bacilli and diphtheria bacilli were rich in antigen reacting with antituberculous serum, avian and piscine type tubercle bacilli and paratubercle bacilli had a moderate concn., while cryptococci and pneumococci were lacking in such antigen. The MeOH ext. equalled the antigen of Besredka in activity. It proved to be rigorously specific; exceptionally it reacted with syphilitic sera, but in these cases tuberculosis could not be ruled out. The MeOH ext. is more active than the EtOH product and can be kept indefinitely in the absence of air, light and moisture.

E. R. LONG

Research on the theory of anaphylaxis. ERNEST PESCI. Turin. *Ann. inst. Pasteur* **35**, 315–20(1921).—Since a given antiserum may react with its antigen in the

ninhydrin test, and yet not confer passive sensitization, and *vice versa*, it may be concluded that anaphylactic shock is not in relation with parenteral digestion. It is known that the no. of blood platelets takes a tremendous drop in anaphylactic shock. Substances which suppress shock, like Na oleate, do so probably through modifications they produce in reaction and consequently in the elec. state of the colloids. Shock is explained as follows. The antigen undergoes gradual transformation into living colloid, stimulating the cells to the synthesis of identical protein with a physical affinity for the same antigen. This new substance is abundant in plasma and certain tissues. The antigen on second injection flocculates this colloid. Intravascular flocculation causes conglomeration of platelets and resulting capillary thrombosis, causing characteristic effects in lungs, liver, or head in different animals. Also in *J. physiol. path. gén.* **19**, 226–41, 242-9(1921). E. R. LONG

The alkali reserve of the blood plasma during protein shock. A. A. EGGSTEIN. Manhattan Eye, Ear and Throat Hosp. and Columbia Univ. *J. Lab. Clin. Med.* **6**, 481–6 (1921).—The alk. reserve of the blood plasma is greatly reduced in shock following the intravenous injection of toxic proteoses and typhoid vaccines in dogs and man. A definite relationship exists between the decrease in the alk. reserve of the plasma and the lowered blood pressure in toxemic shock. When the alk. reserve of the blood falls below 30%, following protein shock, the animal's life is in danger. The administration of $NaHCO_3$ preliminary to the injection of a toxic protein retards the fall of blood alkalies to this critical point. When the alk. reserve has been lowered in protein shock, it can be restored by the intravenous adminstration of $NaHCO_3$, which apparently relieves distressing symptons. E. R. LONG

Studies on the resistance of the red blood cells. II. The resistance of the red blood cells in disease to the hemolytic action of sapotoxin. CHAS. H. NEILSON AND HOMER WHEELON. St. Louis. Univ. School of Med. *J. Lab. Clin. Med.* **6**, 487–504 (1921); cf. *C. A.* **15**, 2492.—Pregnancy is associated with an increased resistance of red cells to sapotoxin. Malaria as such does not lower their resistance, but the administration of quinine to malaria patients does. Quinine does not have this effect on normal corpuscles. Pulmonary tuberculosis increases cell resistance. Typhoid fever has little effect. The relationship of jaundice and blood cell resistance to sapotoxin is very variable, obstructive jaundice often causing a marked increase in resistance and hemolytic jaundice being associated with the reverse. Anemia as such does not affect cell resistance, although the processes that cause the anemia may. Arteriosclerosis is associated usually with an increased resistance of the red cells to sapotoxin. Malignant growths as such have little effect. In general the resistance of the red cells to sapotoxin parallels the cholesterol content of the serum. E. R. LONG

Leuco-agglutinins. M. WEINBERG AND LÉON KEPINOW. *Compt. rend.* **172**, 880–2(1921).—The leucocytes were obtained by injecting into the peritoneal cavity of the guinea pig 5 cc. of a 10% sterilized emulsion of Mellin's food. It is preferable to sensitize by a previous injection of 1 cc. of the same substance. The animal is bled white in 14 to 16 hrs. after the injection, an opening is made in the abdominal cavity and 30 to 40 cc. of 1% soln. of $Na_2C_2O_4$ introduced. The peritoneal exudate, rich in leucocytes, is removed by means of a bulb pipet. Preserved in the ice box it can be used several days. Sometimes leucocytes agglutinate more readily 24 hrs. after prepn. To apply the prepn., 0.3 to 0.5 cc. of the leucocyte emulsion is added to a series of tubes containing 1.7 to 1.5 cc. physiol. saline, then decreasing amts., 0.3, 0.2, 0.1, etc., of the toxin studied are added, the mixt. is shaken and placed in a thermostat for 2–3 hrs. at 37°. During this period each tube should be covered with the thumb and inverted once or twice. Leucocytes have a natural tendency to agglutinate but never with the intensity observed after the action of the toxin. The toxins examd. were those from *B. perfringens* var.

septic, *B. sporogenes, B. aerofetidus, B. histolyticus, B. tetani, B. proteus, B. diphtheritic, B. de Pfeiffer*, staphylococcic and pneumococcic. The pneumococcic, diphtheritic and var. septic show the most active agglutination. Sporogenes and histolyticus are nearly inactive. The leuco-agglutinin is destroyed by heating on the water bath at 58° to 60° for 30 min. L. W. RIGGS

Anaphylaxis and finality. CH. RICHET. *Scientia* 29, 275–80(1921).—R. gives a review and theoretical discussion of the nature and causes of anaphylaxis. L. W. RIGGS

Relation between the amount of stainable lipoid material in the renal epithelium and the susceptibility of the kidney to the toxic effect of the general anesthetics. WM. DE B. MACNIDER. Univ. N. C. *J. Pharmacol.* 17, 289–323(1921).—In normal animals of different age periods there has been demonstrated a larger amt. of stainable lipoid material in the kidney of old dogs than in the kidneys of puppies and young dogs. The distribution also varies with the age of the animal. When normal animals of different age periods are anesthetized by either $CHCl_3$ or Et_2O, there exists a definite relationship between the toxicity of the anesthetic for the renal epithelium and the age of the animal. They are more toxic for the kidneys of old animals than for young ones and $CHCl_3$ is more toxic for the kidney than is Et_2O. The general toxic effect is shown by a disturbance of the acid-base equil. of the blood, which is more marked in the case of $CHCl_3$. These and other results indicate a definite relationship between the amt. of stainable lipoid material in the renal epithelium of both normal and naturally nephropathic animals and the susceptibility of this epithelium to the toxic effects of both ether and $CHCl_3$. C. J. WEST

LINOSSIER, G.: **Les lipoides dans l'infection et dans l'immunité.** Paris: J. B. Baillière et Fils. 105 pp. 10 fr. For review see *Rev. sci.* 59, 380(1921).

H—PHARMACOLOGY

ALFRED N. RICHARDS

Methanol on trial. GIAMBATTISTA FRANCESCHI. *Giorn. farm. chim.* 69, 85–9 (1920).—In the numerous cases where death has resulted from drinking MeOH, the latter was invariably the crude product. Crude MeOH may contain as low as 50% MeOH, the remainder being acetone, and varying amts. of MeOAc, aldehydes, methylacetals, C_4H_9OH, higher ketones, empyreumatic substances, and pyridine bases. Pure MeOH is no more toxic than EtOH. The author has administered daily doses of 32 g. MeOH for extended periods without causing the slightest indisposition. The oxidation products, CH_2O and CH_2O_2, could not be demonstrated after ingestion of MeOH. A. W. DOX

Chaulmoogra oil in leprosy and tuberculosis. The successful treatment of leprosy by injections of soluble preparations of the fatty acids of chaulmoogra and other oils and its bearing on the tuberculosis problem. LEONARD ROGERS. London. *Lancet* 1921, I, 1178–80.—A recent exptl. investigation has been made of the 3 new prepns., which have proved effective in the treatment of leprosy, in animals infected with tuberculosis; but in the acute general tuberculosis produced in the very susceptible animals used the results were entirely negative, except for an early febrile reaction followed by a fall in temp., in 2 goats, who eventually succumbed to the infection at about the same time as a control animal. It is pointed out that these animal infections are equivalent to acute general tuberculosis in man, so that the failure in such cases does not prove the drug to be useless in the more chronic forms of tuberculosis which form the great majority of human cases. E. B. FINK

A new general anesthetic: its theory and practice. R. L. MACKENZIE WALLIS AND C. LANGTON HEWER. St. Bartholomew's Hosp. *Lancet* 1921, I, 1173–81.—Investigation disclosed that the anesthetic properties of Et_2O were largely due to certain

ketones contained in it. Good anesthetic ethers, free from aldehydes, mercaptans, etc., when treated with finely divided permanganate, yielded a pleasant-smelling residue instead of the evil-smelling residue previously obtained. This residue proved to contain ketones, and these compds. appeared to be the essential element in the production of a good and safe anesthetic. The mixt. of ketones proved to be very potent and it was necessary to use a volatile solvent. In view of the readiness with which ordinary Et_2O can be purified, this compd. was selected as the solvent. Into this pure Et_2O the mixed ketones were placed in varying proportions, and the mixts. so obtained were found to be capable of producing anesthesia. The anesthetic action was enhanced if the mixed ketones were first treated with CO_2 and ethylene. The ketones used comprize those in the middle of the series, and a loose chem. combination between these substances and the CO_2 and ethylene apparently results. E. B. FINK

The influence of dilution on the toxic action of alcoholic liquids. H. M. VERNON. *Brit. J. Inebriety*, **18**, 39–76(1920); *Physiol. Abstracts* **5**, 428–9.—Fifty-seven expts. are described on the effect of alc. of different dilns. taken $3^1/_2$ hrs. after food with the day's routine standardized, the effects being judged by target pricking and typewriting tests. Typing time and mistakes are increased by alc., but for comparison the time variable is eliminated by reducing mistakes to const. typing speed. Tables are given of the effects of alc. of different dilns. taken as whisky, beer, cider, claret, with curves showing time of maximal effect, etc. More dil. solns. are more rapidly absorbed and less toxic. The effect of any given percentage increases very rapidly with the quantity taken. For practical purposes 3% alc. as beer and 3% cider are non-intoxicating; there is a distinct gap between 3 and 4% beer, while 5% beer is more toxic than 5% whisky. H. G.

The excretion of silicic acid in the urine after administration of certain silicic acid preparations. F. ZUCKMAYER. Hamburg. *Therap. Gegenw.* **61**, 344–50(1920); cf. Kühn, *C. A.* **14**, 2823.—The following prepns. were used: (1) an infusion of *Herba equiseti*, Galeosidus and Polygoni (Kobert, *Tuberculosis* No. 10–11; Kühn, *Therap. Monats.* **1919**, No. 16; *Münch. med. Woch.* **1918**, No. 52); (2) fresh colloidal SiO_2 soln.; (3) colloidal SiO_2-protein; (4) colloidal SiO_2-casein metaphosphate. These were administered in 1 dose in amts. calcd. to yield 0.2 g. SiO_2. SiO_2 of the urine was detd. and the increase due to the SiO_2 prepn. calcd. The largest increases, 0.10 to 0.14 g., followed the use of (2), the others producing less than half so great an increase. However, the increase following the use of (4) continued over 2 or 3 days. The administration of $CaCl_2$ or of a prepn. of $Ca_3(PO_4)_2$ and protein diminished the excretion of SiO_2 in the urine. I. GREENWALD

The effect of pituitary extract on the rate of urine formation in man. R. MCBRAYER. *N. Y. Med. J.* **114**, 53–5(1921).—In a series of well planned and executed expts. on 7 persons McB. shows that during the first hr. following the hypodermic injection of medicinal doses of pituitary ext. the urine output is markedly decreased. The output of urinary solids is likewise decreased both absolutely and relatively. There also occurs a marked and const. decrease in the systolic, diastolic and pulse pressures, and pulse rate, which decreases appear definitely related to the decrease in the fluid and solid output of the urine. F. S. HAMMETT

Diphtheria carriers and their treatment with mercurochrome. GEORGE A. GRAY AND BERTHA I. MEYER. Mare Island, Cal. *J. Infect. Diseases* **28**, 323–6(1921).—The % of diphtheria carriers found conforms to that found by Labit of the French army for men in a diphtheria environment. The germicide of choice in treating diphtheria carriers is a soln. of mercurochrome-220 in 0.5, 1 or 2% strength. By using this drug 88 of 90 carriers were made carrier-free following an av. of 19.1 applications of this soln. with an av. of only 12.7 sick days, as compared to an av. of 23 days. J. H. L.

The influence of chaulmoogra oil on the tubercle bacillus. JOHN A. KOLMER,

LUTHER C. DAVIS AND RUDOLPH L. JAGER. Philadelphia. *J. Infect. Diseases* **28**, 265–9 (1921).—Undil. chaulmoogra oil (*Taraktogenous kurzii* King) and dilns. in paraffin oil had no appreciable germicidal influence *in vitro* on a strain of bovine tubercle bacilli, according to the results observed with the technic employed in these expts. The Na salts of the total acids of this oil (chaulmoograte) were not included in this study. Undil. and dil. chaulmoogra oil had no appreciable germicidal effect on virulent tubercle bacilli as detd. by an *in vitro-vivo* method employing guinea pigs. Chaulmoogra oil in doses of 0.2 cc. per 100 g. of body wt. administered by intramuscular injection at weekly intervals (equivalent to 2 cc. per kg. or 120 cc. per 60 kg.) had none or but slight effect on the course of tuberculosis in infected guinea pigs. Chaulmoogra oil is relatively nontoxic for guinea pigs; animals have borne at least 11 intramuscular injections of 0.2 cc. per 100 g. without deleterious effect except localized inflammatory changes at the sites of injection. JULIAN H. LEWIS

The inhibitory action of copper salts on pathogenic bacteria. V. LINDÉN. Bonn. *Centr. Bakt. Parasitenk. I Abt.*, **85**, 136–66(1920).—There is a great variation in the sensitivity of different bacteria to Cu. The presence of protein in the culture media reduces the action of Cu except with the tubercle bacillus in which it seems to enhance the action. While a 1:1,000,000 concn. of Cu inhibits tubercle bacilli in a medium contg. protein, they will resist a much higher concn. in an aq. soln. The sensitivity of tubercle bacilli to Cu was so great that a strain was lost by growing in tubes that had been used to contain Cu. Tubercle bacilli when grown on a solid medium containing Cu are colored green, then brown. Staphylococci are the least injured by Cu. The action of Cu against these organisms is enhanced by the addition of methylene blue. The most sensitive (excepting the tubercle bacillus) were the cholera-vibrio El Tor and the typhoid bacillus. Intermediate were paratyphoid B and dysentery (Shiga-Kruse). The concn. of a Cu salt was of less significance in inhibitory expts than the relation between concn. and no. of bacteria. With most bacteria Cu-lecithin as an emulsion in media was the most active Cu compd. With the vibrio El Tor and *Staphylococcus aureus* dimethylglycocoll-Cu was the most active. Far less active was charcoal satd. with Cu salts It was impossible to carry over the results of test-tube expts. to animal expts. However, in one expt. with paratyphoid B, white mice previously treated with Cu lived longer than controls not treated. JULIAN H. LEWIS

Trinitrotoluene poisoning—its nature, diagnosis, and prevention. CARL VOEGTLIN, CHARLES W. HOOPER AND J. M. JOHNSON. U. S. Public Health Service, *Hyg. Bull.* **126**, 7–182(1920).—In this paper exptl. TNT poisoning in animals and poisoning among the workers in explosive factories are studied. For the exptl. work dogs were used. TNT was administered by mouth, injected subcutaneously dissolved in oil, or introduced directly into the lower air passages over long periods of time. By either route the TNT was well absorbed. The symptoms produced were cyanosis, incoördination, vomiting, anemia, marked icterus, salivation, choluria and diarrhoea or constipation. While the complete fate of TNT in the body is not known it is known that it is not excreted as such but usually as a conjugation of its hydroxylamine deriv. with glucuronic acid. On post-mortem the animals showed evidences of anemia icterus, hyperplasia of the spleen and bone marrow. The spleen, bone marrow, liver and lymph glands contain a large amt. of hemosiderin, as the result of a very acute hemolysis. This hemolysis is probably the result of the formation of methemoglobin, injuring the red cells which are then destroyed in the above organs. A marked individual and species variation was observed in the susceptibility of the dogs. A definite tolerance to the poison was never established. Field investigation among TNT workers showed that 7?% were suffering from anemia. These all showed the Webster test. Cyanosis, pallor, and dermatitis were seen. The poison may be absorbed by the skin, lungs,

or gastro-intestinal tract. Diet seems to be an important factor in the occurrence of TNT poisoning. JULIAN H. LEWIS

Chaulmoogra oil in the treatment of tuberculosis. WILLIAM L. CULPEPPER AND MARJORIE ABLESON. Detroit. *J. Lab. Clin. Med.* 6, 415–26(1921).—Expts. in treatment with the Na salts of four fractions of the acids of chaulmoogra oil were made on 50 guinea pigs. Peritoneal administration was found to produce no undesirable effects. The acid Na salts were bactericidal to tubercle bacilli in a concn. of 1:10,000. Of 12 pigs inoculated with tuberculosis and not treated with the chaulmoogra oil acids, all died but one; of 12 similarly inoculated, but treated, pigs, only one died of tuberculosis. There was a marked difference in pathological findings in favor of treated pigs. Treated pigs showed an average gain of 49 g. over non-treated pigs in equal time. The administration of drug seemed to favor weight increase. E. R. LONG

The pharmacologic action of lead in organic combination. E. C. MASON. Univ. of Cincinnati *J. Lab. Clin. Med.* 6, 427–53(1921).—$(C_2H_5)_3Pb\text{-}Pb(C_2H_5)_3$ and its salts stimulate the higher centers of the central nervous system, the injection of 0.0025–0.0050 g. producing convulsions in a medium-sized dog. An extreme fall in blood pressure follows the first injection, owing to stimulation of the inhibitory vagus center for the heart, sudden dilatation of visceral vessels, and direct depressant action on the heart. A prolonged rise in blood pressure follows subsequent injections, owing to constriction of visceral vessels and stimulation of the sympathetic nerves to the heart. Respiration is stopped by first injections and increased by subsequent ones. Dyspnea occurs, owing to direct action on the respiratory center. Intestinal activity is increased. Kidney and spleen vols. increase first and then decrease. Subsequent injections produce only decrease. E. R. LONG

Action of bismuth upon syphilis and on the trypanosomiasis of Nagana. R. SAZERAC AND C. LEVADITI. *Compt. rend.* 172, 1391–2(1921).—Tartrobismuthate of Na and K exercizes a curative action upon exptl. syphilis in the rabbit (virus dermotrope and neurotrope) and upon the spontaneous spirillosis (*Spirocheta cuniculi*) of that animal. The administration of 0.06 g. per kg. of guinea pig caused a disappearance of the circulating trypanosomes after 48 hrs.; and a dose of 0.1 g. produced the same result in 24 to 48 hrs. After the latter dose a relapse occurred after 12 to 15 days. Expts. are in progress with other derivs. of Bi. L. W. RIGGS

Alimentary anaphylaxis and its therapeutics. W. KOPACZEWSKI. *Compt. rend.* 172, 1386–8(1921).—Children fed mare's milk, or persons who eat horse flesh are subject to an extremely severe anaphylactic shock, when treated with antidiphtheritic serum prepd. from horses. A case is also reported in which the intravenous injection of "hemoplase de Lumière," made from the red cells of sheep, into a person who has been fed daily with mutton produced extreme reactions which were prevented by the subcutaneous injection of 5 cc. of camphor liniment (huile camphrée) 30 to 40 min. before the introduction of the hemoplase de Lumière. Alkaline carbonates containing a few drops of ether or of 1% sodium oleate can be used in place of the camphor liniment. Before administering serum treatment the kind of food the patient has been eating should be known. L. W. RIGGS

Comparative study on the functioning of the liver after surgical anesthesia by chloroform, ether, nitrous oxide, or novocaine. F. WIDAL, P. ABRAMI AND J. HUTINEL. *Compt. rend.* 172, 1145–9(1921).—The digestive hemoclasis, shown by the leucocyte count after the absorption of a glass of milk, permits the detection of the least functional alteration of the liver. With $CHCl_3$, even in small amts., protopexic insufficience is shown early and remains constant. In 4 cases with anesthesia for 20 to 35 min. the hemoclastic crisis occurred 24 hrs. after the operation in 3 and 48 in one. In the 3 cases mentioned the urine contained neither urobilin nor biliary salts at the crisis.

The duration of postchloroformic insufficience has not exceeded a few days. Ether anesthesia furnishes results much less const. than those observed with $CHCl_3$. In 2 cases of 10 and 18 min. duration the test by digestive hemoclasis was negative. In 26 and 35 min. cases the crisis appeared in 48 hrs. and disappeared 2 and 3 days later, resp. In the 35 min. case there was neither urobilinuria nor excretion of biliary salts. N_2O anesthesia for 35 and 40 min. showed protopexic insufficience after 24 hrs. and continued 3 and 4 days, resp.; both cases were accompanied by urobilinuria and the 40 min. case by the excretion of biliary salts. Shorter periods of N_2O anesthesia, *viz.*, 17 and 24 min., failed to show either protopexic insufficience or retention of biliary salts or pigments. Novocaine failed to produce either the hemoclastic crisis or the least sign of hepatic insufficiency. L. W. Riggs

Effect of small doses of atropine on the heart rate. Hugh McGuigan. *J. Am. Med. Assoc.* **76**, 1338–40(1921).—Atropine sulfate was dissolved in sterile water to make a 0.1 and a 0.2% soln. and injected hypodermically. The heart and respiration rates were counted for 30 or 60 sec. every 5 or 10 min. Six persons were tested, 5 being apparently healthy and one a genito-urinary case. Summary: Small doses of atropine, if they influence the heart rate, only slow it. This slowing is produced by an action on the vagus center in the medulla. There may be some stimulation of the vagus endings. Larger doses (0.001 g.) still cause slowing with a tendency to irregularity. This is the point at which the vagus endings begin to be paralyzed. If the dose is increased to 0.002 g. the primary slowing of the heart rate may be so transient that it escapes notice if the object in giving atropine is to paralyze the vagus endings and release the heart, at least 0.001 g., hypodermically, is necessary. In urgent cases 0.002 g. should be given. L. W. Riggs

Dangers of pituitary extract. M. Pierce Rucker and Chas. C. Haskell. *J. Am. Med. Assoc.* **76**, 1390–3(1921).—Several case histories are given and the following conclusions stated: The evidence indicated that the use of pituitary ext. is accompanied by danger to the mother and to the child. The injurious action on the mother is manifest by an increase in the frequency of perineal lacerations and the occasional occurrence of uterine rupture, *in cases in which all the indications for the use of the ext. are present.* The dangers to the child consist in a greater tendency toward the production of asphyxia and toward the occurrence of intercranial hemorrhage. The circulatory action of the drug is undesirable as it tends to cause tetanus of the uterus in lower animals and also in human beings. While the administration of pituitary ext. may not always result in a catastrophe there is always the possibility of harm even from the so-called "safe" doses. L. W. Riggs

Massive doses of alkali in two cases of impending diabetic coma. Wm. E. Cary. *J. Am. Med. Assoc.* **76**, 1393–5(1921).—"In cases of precoma in diabetes with low reserve of alkali, the symptoms of acid intoxication can be promptly eliminated by immediate recourse to alkali preferably by the mouth but if absolutely necessary by other routes in addition, when no other procedure will avert death. The importance of getting from 25 to 50 g. of the alkali into the body within the first two hrs. is emphasized. The reaction of the urine should be carefully observed, and frequent tests of the urine or blood made to prevent overalkalization. In severe cases the immediate danger of coma passes when the reserve is brought to 30, and conservatism in going to 40 may be wise." L. W. Riggs

Iodine in the cerebrospinal fluid with special reference to iodide therapy. Earl D. Osborne. *J. Am. Med. Assoc.* **76**, 1384–6(1921).—The analytical method of Kendall was used. Conclusions: Iodine is present in the cerebrospinal fluid of normal individuals, and present in increased amt. following the administration of iodides by mouth, rectum and intravenously, being present in much larger amts. in the latter

case. The amts. present plot a definite curve depending on the amt. administered. Certain observations made in the course of this study suggest the possibility that neurosyphilitic tissue takes up more I than normal nervous tissue, and that the presence of a meningitis increases the permeability of the meninges to I compds. in the blood.

L. W. RIGGS

Use of oxygen added to carbon dioxide for subcutaneous injections as treatment of mountain sickness and certain toxic dyspneas. RAUOL BAYEUX. *Compt. rend.* **172,** 1388–90(1921); cf. *C. A.* **14,** 1151, 1934; **15,** 2314.—Two distinct forms of symptoms, which are often confounded, appear in mountain sickness, *viz.*, *asphyxic* and *toxic*. The latter form is attended by nausea, prostration, chills without fever, diminished pulse and respiration, and may terminate in death if the subjects are not removed to lower altitudes. Inhalations of O are very efficacious against the asphyxic form but are without action in the toxic form. B. has described his symptoms with the toxic form in 2 instances, and the relief obtained by the subcutaneous injection of mixts. of O and CO_2. For this purpose the proportions recommended are 85% O and 15 CO_2. L. W. RIGGS

Fatal intoxications by arsenic in viticultural districts. PAUL CAZENEUVE. *Bull. acad. méd.* **85,** 660–71(1921).—Several cases of arsenical poisoning are reported, due to the use of As compds. in the cultivation of grapes. G. H. S.

The action of minute amounts of acid and alkali upon the vessels and organs containing smooth muscle. PAUL HEYMANN. *Arch. exptl. Path. Pharm.* **90,** 27–76 (1921).—The effect of minute amts. of acid and alkali was detd. by perfusion of the Trendelenburg frog prepn. or the isolated rabbit ear with saline or Ringer soln. contg. the test substance. The change in the drop number was noted. In such a frog prepn. perfused with bicarbonate-free Ringer soln. the drop number changed from 70 per min. to 36 per min. after the addition of 0.001 *N* HCl (concn. 1:27,000). Many protocols are presented showing similar changes in response to the addition of HCl in various concns. The change occurs quickly and if the perfusion is not too long continued the reaction is reversible. Similar results were obtained by perfusion of the rabbit ear. The presence of serum in the fluid did not greatly modify the reaction. In the Pissemski prepn. 0.001 *N* HCl caused a very high-grade edema. Other acids, HNO_3, H_2SO_4, H_3PO_4, lactic, acetic, and tartaric, gave similar effects. The edema production was not parallel to the vasoconstricting action, since those acids which gave the greatest edema were weakest in the other respect. Perfusion with hypertonic salt and sugar solns. quickly abolished the vascular constriction. CO_2 caused a vascular dilation in the rabbit ear or frog prepn. but in high diln. it lead to a constriction. Dil. NaOH solns. also caused a decrease in the drop no. as well as an edema. The acids and alkalies were tested upon vessel strips and upon the stomach muscle of the frog. Small amts. stimulated; larger amts. paralyzed. During an acid perfusion the addition of adrenaline, if active at all, caused a dilation; during an alk. perfusion it was without effect. After nerve degeneration or ergotoxin poisoning the effects of acid were weakened or delayed; or, there might be a reverse action. The effect of alkali under these conditions was not modified. Minute amts. of acid or alkali stimulated the surviving intestine; higher concns. destroyed the rhythmic contraction and the tonus. Upon the plexus-free cat intestine acids and alkalies favored contraction. The point of attack for acids and alkalies is the smooth musculature. Acids may primarily stimulate the nervous apparatus but they also exert a secondary paralyzing effect. G. H. S.

Physiological action of allyltheobromine. REMOND AND COLOMBIER. *Bull. acad. méd.* **85,** 592–4(1921).—The repeated injection of allyltheobromine by either the subcutaneous, intramuscular, or intravenous route causes an increase in the secretion of urine and the elimination of urea. G. H. S.

Certain factors connected with the toxicological testing of arsphenamine. G. C.

LAKE. *Am. J. Syphilis* 5, 96–130(1921).—A thorough investigation of the factors that might influence results in the toxicological testing of arsphenamine showed that a false value (increased) may be obtained in a variety of ways. The following may influence the test and give erroneous results. Resistance of the animals may be low; they may have an inherent hypersusceptibility or be actually inferior physically. The method of holding the animals for the injection may lead to abnormal excitation and physical exertion. Pregnant rats receive a relatively larger dose in proportion to the body wt., exclusive of the pregnant uterus. The application of heat in the prepn. of solns. causes the formation of toxic by-products as the result of a rapid oxidation. The addition of an insufficient amt. of alkali in prepg. the soln. may lead to a pptn. of the substance in the circulation. Too rapid a rate of injection favors the production of hemorrhage and thrombosis. The apparent toxicity of arsphenamine may also be increased by employing animals with a heavily loaded digestive tract, or by the use of a soln. in too high a concn. G. H. S.

Effect of barium chloride on the frog heart. S. DE BOER. *Arch. ges. Physiol.* **187**, 283–92(1921).—After intoxication of the frog heart with $BaCl_2$ the refractory stage of the ventricle is lengthened and the ventricular rhythm is halved. The application of an electrical stimulus so alters the ventricular rhythm that it becomes twice as quick as normal. If this shock is applied at a very definite point in the contraction wave a small systole is introduced. In a similar manner the normal rhythm can be transformed by an electrical stimulus to the halved rhythm. In this case the ventricle in the halved rhythm can be thrown into an exaggerated post-compensatory systole. G. H. S.

Differential characteristics of strophanthin and ouabain. A. RICHAUD. *Bull. acad. méd.* **85**, 461–4(1921).—The various properties of strophanthin, $C_{31}H_{48}O_{12}$, are compared to those of ouabain, $C_{30}H_{46}O_{12}$. There is no fixed m. p. for either one, although a m. p. of 180° is given for ouabain and 165° for strophanthin. Soly. tests show that 1 part of strophanthin is sol. in 43 parts of water at 15°; 1 part of ouabain is sol. in 150 parts. This test is the most ready means of differentiation. Ouabain deviates the plane of polarized light to the left, strophanthin to the right. Toxicity tests are an unsatisfactory means of differentiation. In their physiol. effects one point, the character of the tracing of the treated isolated rabbit heart, may be of differential value. G. H. S.

Intraperitoneal infusion in infants with a water depletion. M. WEINBERG. *Z. Kinderheilk.* **29**, 15–35(1921).—Intraperitoneal infusion of Ringer soln., physiol. saline, dextrose solns., or mixts. of dextrose and carbonate solns., can be given at least twice a day without causing any inflammatory processes within the peritoneum or any disturbance of the intestinal tract. Medicinal compds. or dyestuffs can be added to the infusion soln. where indicated. Because of the simplicity of administration and freedom from danger of sepsis the procedure can be carried out very quickly. Shock never occurs. The fluid is adsorbed quickly; 60% within the first hr., and within 24 hrs. an amt. as large as 300 cc. will have disappeared. Improvement in physical condition follows closely upon the introduction of the fluid. Changes in pulse, respiration, general condition, and wt. are manifested. More marked results are noted in diseases of alimentary nature than in those of infectious character. The treatment is of greatest value in intoxications. G. H. S.

Significance of physiological ion antagonisms. S. M. NEUSCHLOSZ. *Arch. ges. Physiol.* **187**, 136–8(1921).—A reply to Handovsky. Cf. *C. A.* **15**, 1237, 1734. G. H. S.

Toxicity of picric acid on the frog and on the rabbit. E. D. BROWN, JACOB AHLFS AND MERRILL HOWARD. Univ. Minn. *J. Pharmacol. Proc.* **15**, 235–6(1920).—The minimum lethal dose, when the drug was introduced into the anterior lymph sack, was

from 0.00015 to 0.00021 per g. frog. The toxic dose for rabbits was 0.125 to 0.279 g. per kg. body wt. The acid is readily absorbed through the intact skin of the frog. Death in the rabbit was sudden and due to cessation of respiration or stoppage of the heart. C. J. WEST

Cumulative action of the digitalis principles. THOMAS S. GITHENS. Mulford Lab. *J. Pharmacol. Proc.* **15**, 239–40(1920).—With both the $CHCl_3$- and H_2O-sol. glucosides, $^1/_8$ of the minimum lethal dose daily did not cause death within 1 mo., whereas daily doses of 0.5 of the min. lethal dose of either killed after 2–3 doses. Using daily doses of 30–40% of the min. lethal dose, no distinct difference in the cumulative action could be brought out by daily hypodermic injections in guinea pigs. In a few instances death seemed to be due to necrosis of the external oblique muscle. C. J. WEST

Toxicological action of ureides of *N*-phenylglycine-*p*-arsonic acid with special reference to the β-methylureide. LOUISE PEARCE AND WADE H. BROWN. Rockefeller Inst. *J. Pharmacol. Proc.* **15**, 240–1(1920).—The mean lethal dose of the ureide computed for 4 species is about 2 g. per kg., which in terms of As would represent 0.4 g. The mean lethal dose of the β-methylureide was found to be approx. 1.25 g. per kg. or an amt. corresponding to 0.2 g. As. Symptomatically, the 2 drugs do not differ greatly in their toxic action. C. J. WEST

Therapeutic action of ureides of *N*-phenylglycine-*p*-arsonic acid in trypanosome and spirochete infections. LOUISE PEARCE AND WADE H. BROWN. Rockefeller Inst. *J. Pharmacol. Proc.* **15**, 242–3(1920).—Doses of 1 g. ureide per kg. given intraperitoneally and 0.6 g. intravenously were uniformly curative in mice infections; 0.75 g. per kg. in rats intraperitoneally and 0.5 g. intraperitoneally in guinea pigs (for infections with *Tr. brucei*). Doses of 0.225 g. of the β-methylureide intraperitoneally in mice were uniformly curative, 0.5 g. in rats, and 0.3 g. in rabbits. Infections with *Sp. obermeieri* and *Sp. novyi* and exptl. *Treponema pallidum* infections were also studied. C. J. WEST

Evidence for the presence in digitalis of a principle that is eliminated rapidly after intravenous injection into the cat. M. S. DOOLEY. Cornell Univ. Med. College. *J. Pharmacol.* **17**, 277–88(1921).—Evidence is submitted to show that the total amt. of digitalis required to cause death is less when this amt. is injected within a few min. than that required when the administration is prolonged over a period of several hrs. The evidence that the substance has a true digitalis action is afforded by the fact that it is synergistic with other digitalis substances, such as ouabain. The results are interpreted as indicating the presence in the leaf of digitalis of a substance having a shorter period of cardiac action in the cat than that of any true digitalis substance hitherto studied in this way. This brief period of cardiac action is regarded as evidence for its "elimination," that is, when it has ceased to exert its typical effect, even though there may be no definite proof of its destruction or excretion from the body. There is some clinical evidence in support of this view. C. J. WEST

Constituents of Lathyrus sativus seeds and their action. WALTER J. DILLING. Glasgow Univ. *J. Pharmacol.* **14**, 359–66(1920).—*Lathyrus sativus* seeds contain starch, cane sugar, legumin vicilin, legumelin, a fixed oil, a gum resin, and an oleoresin, the last 3 in small amts. only. The active principle of the seeds consists of 2 alkaloids, which differ slightly in their action and are separable by the Stas-Otto process in groups II and IV. The max. yield of the 1st is 0.0094 %, of the 2nd 0.0035 %. The characteristic action of both alkaloids in frogs is the early production of paresis due to an action on the central nervous system, probably in the brain. Other effects are given. C. J. WEST

Pharmacological action of subdural injection of tricresol serum. A. E. LIVINGSTON. Div. Pharm., Hyg. Lab. *J. Pharmacol. Proc.* **15**, 247–8(1920).—The results furnish

a direct proof of the conception of some investigators that when a moderate amt. of tricresol serum is slowly injected subdurally the resulting fall in blood pressure and stoppage of respiration are due not to an increase in cerebrospinal fluid pressure, but to some toxic property of the PhOH deriv. C. J. WEST

Anaphylactoid phenomena from the intravenous administration of various colloids, arsenicals and other agents. PAUL J. HANZLIK AND HOWARD T. KARSNER. Western Reserve Univ. *J. Pharmacol.* **14**, 379–423(1920).—Mild Et_2O anesthesia and the intravenous injection of normal saline are practically harmless to the circulatory and respiratory systems of guinea pigs, but the remaining 29 agents studied were found to be distinctly harmful in varying degrees. The injury produced by the intravenous injection of the following agents is expressed through the respiratory system; they produce definite anaphylactoid symptoms, and pulmonary distention, congestion, hemorrhages, and thrombi without definite cardiac dilatation: 0.5% agar sol, 0–5% agar gel, 1:4 and 1:6 agar sol-gel, dog bile, human serum and typhobacterin. The following agents produce definite symptoms of respiratory distress with pulmonary congestion and hemorrhages but, as a rule, no distention and thrombi: althea ext., arsphenamine, collargol, Congo red, dextrin, gelatin, inulin, neoarsphenamine, phylacogen, rabbit serum, Na arsenate and venarsen. The following agents injure the circulatory and respiratory systems as indicated by the presence of anaphylactoid symptoms, pulmonary distention, congestion and hemorrhage together with cardiac dilatation: acacia, plain, dialyzed and toxified with rabbit's serum, beef serum, glycogen, nuclein solns., pancreatin, peptone, pollen ext., and starch. The results obtained are decidedly against the promiscuous and unwarranted use of the intravenous method of administering drugs as a routine therapeutic measure. The results indicate that it is quite erroneous to regard the disturbances produced by the intravenous injection of sundry agents in the same category with true anaphylaxis. C. J. WEST

Effects of various colloids and other agents which produce anaphylactoid phenomena on bronchi of perfused lungs. PAUL J. HANZLIK AND HOWARD T. KARSNER. Western Reserve Univ. *J. Pharmacol.* **14**, 449–61(1920).—Perfusion of the lungs of guinea pigs with agar sol-gel (1:6) causes prompt and marked distension of the lungs and stoppage of the perfusion flow owing to the massing of agar emboli in the pulmonary vessels. Prompt distension of perfused lungs occurs with peptone and histamine, but in the absence of pulmonary emboli, and this is due to active stimulation of bronchial muscle. The mechanism of agar action consists of a passive bronchoconstriction by compression of bronchioles from emboli in the pulmonary vessels. This is also the chief mechanism in the marked pulmonary inflation produced by agar in intact guinea pigs. C. J. WEST

Effects of various colloids and other agents which produce anaphylactoid phenomena on surviving intestine and uterus. PAUL J. HANZLIK. Western Reserve Univ. *J. Pharmacol.* **14**, 463–78(1920).—The direct application of agar sol and agar gel to surviving intestine and uterus produces either no effect or slight depression of peristalsis. The following agents depressed the peristalsis: acacia, dextrin, glycogen, gelatin, starch, human and horse serums, and nuclein soln. Peptone and rabbit serum produced moderate to marked stimulation. Beef serum was irregular. Congo red in low concn. produced definite and rather marked stimulation. This study supports the contention elaborated in previous papers as to bronchial musculature, that the disturbances produced by intravenous injection of agar bears no relationship whatever to anaphylaxis. C. J. WEST

Comparison of the prophylactic effects of atropine and epinephrine in anaphylactic shock and anaphylactoid phenomena from various colloids and arsphenamine. PAUL J. HANZLIK AND HOWARD T. KARSNER. Western Reserve Univ. *J. Pharmacol.* **14**,

425–47(1920).—The intravenous injection of atropine in guinea pigs in doses of 0.01 mg. per g. body wt. can completely prevent the toxic effects produced by the injection of beef serum and peptone in doses corresponding to those used in the proteose therapy of Nolf; partial protection was obtained against the effects of agar sol, agar sol-gel, arsphenamine, Congo red, peptone serum sensitization and typhobacterin. No protection was obtained against the effects of acacia, althea, dextrin, pollen ext. and starch. When injected intravenously together with the antigen or immediately preceding it, epinephrine in doses of 0.0005 cc. of 1:10,000 per g. body wt. prevents death from true anaphylactic shock in guinea pigs. It exerts no protection against the effects of agar sol. agar sol-gel, dextrin, peptone, and starch, when injected after or too long before the antigen in serum-sensitized animals. On the basis of this work, the mechanism of agar and similar agents bears no relationship to true anaphylaxis or anaphylactic shock.

C. J. WEST

Report of the Committee on Occupational Diseases in the Chemical Trades (BASKERVILLE) **13.**

I—ZOÖLOGY

R. A. GORTNER

Physiology of the silkworm. A. P. JAMESON AND W. R. G. ATKINS. *Biochem. J.* **15**, 209–212(1921).—The H-ion concn. by the method of Clark and Lubs (*C. A.* **11**, 3288) and the enzymes in the digestive tract were examd. (See also Sawamura, *Bull. Coll. Agr. Tokyo* (Imp. Univ. Japan) **4**, (1900–1902).) The p_H of the silkworm, *Bombyx mori* = 6.8, and that of the silk gland is very similar. The p_H of the digestive secretion = 9.0–9.8; that of the hind-gut = 8.4 The p_H of the moth = 5.2–5.8. A diastase, active in strongly alk. soln., and a maltase are present in the digestive juice of the silkworm. A feeble maltase and a more active invertase are present in the blood or hemocelic fluid. Oxidases are absent from both blood and digestive juice, but catalase action is shown by both. BENJAMIN HARROW

The vitality of Actinia bermudensis: a study in symbiosis. JOHN F. FULTON, JR. Bermuda Biol. Sta. *J. Exptl. Zoöl.* **33**, 353–64(1921).—This sea anemone is remarkably resistant to unfavorable environmental conditions. In sea water, it lived 6 days when sealed in a vol. of 100 cc. and kept in sunlight; under the same conditions but in darkness, it lived 5 days. In the air (unsealed), it lived 7 and 6 days, respectively, in sunlight and darkness; in 100 cc. CO_2 (sealed), 45–48 and 40–45 hrs., resp.; in 100 cc. O_2 (sealed), 7 days in sunlight and darkness; in 100 cc. air (sealed), 11 and 7 days, respectively, after which the expts. were discontinued. The gastrovascular fluid of this anemone contains a flagellate, *Zoöxanthella*, which does not seem to assist *Actinia* in resisting unfavorable conditions The association of the two organisms is probably one of obligate parasitisms, *Actinia* being parasitic upon *Zoöxanthella*. CHAS. H. RICHARDSON

An experimental study on glochidia and the factors underlying encystment. LESLIE B. AREY. Northwestern Univ. Medical School. *J. Exptl. Zoöl.* **33**, 463–98(1921).—Glochidia are immature forms of fresh water mussels which live ectoparasitically on fishes. Most of the expts. described in this paper were made upon the glochidia of *Lampsilis luteola*. The glochidia reacted to appropriate concns. of acids (HCl, acetic, picric), alkali (KOH), alcs. (methyl, ethyl), sugars (dextrose, sucrose), salts (KCl, KBr, KI, NaCl, LiCl, $MgCl_2$, $CaCl_2$). "The activation is ionic, not osmotic. Subminimal chem. solns. do not notably increase irritability and thereby lower the threshold to touch." The tactile response of the parasite is adequate to insure attachment to the host. There are other physiol. and biol. considerations. CHAS. H. RICHARDSON

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The detection and estimation of saccharin and benzoic acid in foods. J. GROSSFELD. *Z. ges. Kohlensaure Ind.* **26**, 143–4, 159–60(1920); *Chimie and industrie* **5**, 579(1921).—BzOH is extd. with Et_2O and identified by means of Mohler's test as modified by Heide and Jacob and then by G. The Et_2O ext. is shaken with an alk. soln., evapd., heated for 20 min. on a water bath in the presence of 0.1 g. of KNO_3 and 1 cc. of concd. H_2SO_4, cooled, 2 cc. of water added, cooled again, and treated with 10 cc. of 15% NH_3 and then 2 cc. of a 2% soln. of hydroxylamine hydrochloride. The rate at which the red coloration develops depends on the amt. of BzOH present. This reaction is characteristic of C_6H_4 derivatives, including saccharin. When the two are present, they are extd. together by shaking 6 times with an equal vol. of Et_2O; after evapn. the BzOH is removed from the residue by extg. with four or five 10 cc. portions of CCl_4. The CCl_4 ext. is dild. with an equal vol. of alc., and the BzOH is titrated with 0.1 *N* NaOH. The saccharin is detd. by its sweetening power and by detns. of S and N. If salicylic acid is present along with the BzOH, the alc. CCl_4 mixt., after titration, is evapd., to dryness on the water bath, dissolved in water, and an aliquot containing about 10 mg. of residue is treated according to Mohler's test, as modified by G. The color is compared with that produced in 10–11 cc. of 2% KCNS by the addition of known amts. of ferric ammonia alum. 0.1, 0.5, 1, 2, 3, 5, 8, 10 mg. of BzOH correspond to 0.006, 0.027, 0.048, 0.060, 0.080, 0.0110, 0.185, 0.2 mg. of Fe_2O_3. The phenolphthalein added for the titration of the acidity hardly interferes with the reaction. A. P.-C.

Report upon the methods used for the inspection of canned foods and their reliability for this purpose. I. Canned meat. WILLIAM G. SAVAGE. Dept. Sci. Ind. Research, Food Invest. Bd., *Spec. Rept.* **3**, 23 pp.(1920).—The report deals with canned meats imported into England, considering how the methods employed in canning affect the physical properties of the cans. Usually 10% of the shipment is examd. for well-defined holes, marked indentations, or other signs of gross ill-usage, rust and "blowing." The cans are also inspected by percussion, which should produce a dull note all over, and by shaking, which shows if contents are "sloppy." The methods are discussed at length. Comparative study was made at 5 ports in 73 cases of the actual bacteriol. and chem. condition found when cans were opened to det. the reliability of the inspection. Out of 16 samples passed and 57 rejected the respective nos. found to contain good and sterile meat were 15 and 31; good meat not sterile 0 and 11; unfit meat 1 and 15. The % of cases in which sound edible meat was found in rejected samples was raised through disqualification of "leakers," wherein the fault is usually with the can and not its contents. Naked-eye inspection of the contents was found to be all that is required if the method of inspection needs to be changed. H. A. LEPPER

The bacteriology of canning. F. D. FARRELL. Kansas Agr. Expt. Sta., *Directors Rept.* **1918–19**, 76.—Directions for canning asparagus are given. The data show that the addition of more than 1% of salt or 0.05% of acid decreases the time of processing necessary to prevent spoilage, but injures the flavor and palatability of the asparagus. J. J. SKINNER

Swells in canned foods. H. SERGER. Brunswick. *Z. Nahr. Genussm.* **41**, 49–68 (1921).—A review of the various types of spoilage found in canned food. Several devices are described for *testing cans for leaks* most of which are based on the admission of a liquid through leaks from the outside to the interior of the can under test by means of suction. An *apparatus for collection* and *qual. analysis of* the *gas* from a swell is described. This consists in a device for puncturing the can, collecting the gas over water, thence admitting the gas into an evacuated vessel containing small dishes of $Pb(C_2H_3$-

$O_2)_3$, lime water, and Nessler's reagent, respectively. The gas remains in contact with the reagents for 12 to 24 hrs. after which the presence of H_2S, CO_2, or NH_3 can be ascertained by observation of the reagents. L. D. ELLIOTT

Cause of the rusting through of canned food containers of tinplate. F. v. MORGENSTERN. Brunswick. *Z. Nahr. Genussm.* **41**, 175–8(1921).—Many cases of corrosion and pinholing of cans have occurred in Germany since the war period began. Part of the trouble is attributed to the inferior tin coating now employed. The quantity of Sn per 100 sq. cm. which before the war was 0.3 g. is now often only one third that amt. Several lots of pipholed peas and beans were investigated. In some cases the contents of the leaking cans were spoiled and in other cases apparently normal. The interior of the affected cans were found to be studded with small knobs the size of a pin head underneath which were invariably found depressions eaten into the tin. The material forming the cap or knob over the depressions was found to be a nitrogenous, probably albuminous, compd. combined with Fe. An examn. of the interior of unaffected cans disclosed numerous small eruptions which were found to be filled with small black crystals, thought by M. to be graphite, or a highly carbonaceous Fe compd. M. advances the theory that electrolysis takes place at these flaw spots in the tinplate bringing Fe into soln. which subsequently forms an insol. nitrogeneous compd. covering these spots. This compd. may finally become thick enough to protect the contents of the can even though the hole may finally pierce the can. L. D. ELLIOTT

A deficiency in the lead-zinc law of June 25, 1887. F. M. LITTERSCHEID. *Z. Nahr. Genussm.* **41**, 132–6(1921).—A discussion of the law relating to metal food containers. L. D. ELLIOTT

Rangoon-beans as human food. ROBERT COHN. *Chem. Ztg.* **45**, 86–7, 101–2 (1921).—A reply to the article of Berg (*C. A.* **14**, 3113). The discarding of the wash H_2O and H_2O used for cooking beans 1 hr. causes a loss of 15% of nutritive value as N substances and carbohydrates, 10% of N substances alone and 50% of total ash. H. A. LEPPER

Apparatus for keeping bread fresh. J. R. KATZ. *Chem. Weekblad* **18**, 317(1921).—An app. for keeping bread fresh is designed to keep the loaves, after cooling, in a stream of air humidified by contact with a soln. of KCl. This app. has been used with success in various bakeries, and is entirely practicable. NATHAN VAN PATTEN

Larvae in bread. Corncockles in flour. K. KRAFFT. *Z. Nahr. Genussm.* **41**, 75–8(1921).—Numerous living yellow worms under the crust of a sample of black bread were identified as the larvae of the moth *Endrosis lacteella* Schiff. Several flours composed of varying mixts. of wheat, rye, and barley caused illnesses due to the presence of particles of corncockle in the flours in amts. of about 1%. L. D. ELLIOTT

Artificial leavening agents for bread. ANTONIO CERIOTTI. *Anales soc. quim. Argentina* **8**, 118–32(1920).—A general discussion. L. E. GILSON

The relation of ash and gluten in wheat flour. H. E. WEAVER. *J. Am. Assoc. Cereal Chem.* **6**, No. 2, 11–13(1921).—Analysis and baking tests of mill streams of flour shows that the greater ash is contained near the bran coat, the best bread is obtained from the crushes lowest in ash, and the gluten increases as the ash increases. In the break flours the relation between gluten and ash disappears. The best and purest flour contains the least ash provided the streams are handled properly. The ash test is important to the miller as it is the best indication of the uniform action of the mill day by day. Comparison on 10 samples of Kansas hard wheat did not indicate that high ash follows high gluten in the milled flour. H. A. LEPPER

The use of color mixtures as an aid in microscopy. P. P. FECHNER. Düsseldorf. *Z. Nahr. Genussm.* **41**, 170–2(1921).—F. describes color reactions obtained in the *examn. of flour mixts.* by using his color mixt. called "violet" and a "black-white-red"

mixt. similar to Herter's (*Z. ges. Getreidew.* 7, No. 2(1915)). The compn. of the reagents is not given. L. D. ELLIOTT

Glutinized maize bran. G. CONSOLANI. *Il. Coltivatore* 66, No. 1, 10–12; *Bull. Agr. Intelligence* 11, 343–4.—Glutinized maize bran is that which remains of the grain after the starch has been extd. from it. The process of manuf. is described. The analyses (%) of whole maize, maize bran and glutinized maize bran are, resp., H_2O 13.00, 13.20, 9.40; protein 9.88, 14.10, 23.99; digestible albumin 6.6, 9.8, 18.6; N-free ext. 69.24, 56.00, 47.37; fat 1.40, 3.70, 13.05; ash 1.30, 5.80, 1.36; cellulose 2.18, 7.20, 4.83; nutritive ratio 9.44 : 1, 4.6 : 1, 3.7 : 1; com. units 93.70, 83.57, about 130. Excellent food especially for fattening cattle and pigs, and for milch cows, young animals and poultry. H. A. LEPPER

Manihot flour. CLEMENS GRIMME. Hamburg. *Z. Nahr. Genussm.* 41, 172–5 (1921).—Analyses of *Manihot utilissima* Pohl and *M. palmata* Mueller and of flour therefrom. The ash of the *Manihot* root is characterized by its high K and P content. The thickening power of manihot starch was found to lie close to that of corn starch, a little higher than rice and palmsago and somewhat lower than arrowroot and potato starches. L. D. ELLIOTT

Reductase test for the purity of milk, in dairy practice. CHR. BARTHEL. *Le lait* 1, 62–66(1921).—B. discusses the value of the reductase test for milk (decolorization of methylene blue) without presenting new data. He decides that the array of evidence signaling the reliability of the test as proposed and as practiced in the several dairy countries is sufficient to overcome O. Rahn's criticism against its value. Rahn's criticism was directed chiefly against the interpretation of the reduction effect. H. F. Z.

Lactic ferments. GORINI. Milan. *Le lait* 1, 57–62(1921).—G. reviews his work on lactococci and lactobacilli and calls attention to the proteolytic activity of the group of bacteria widely known as *Streptococcus lacticus*. The influence of heat on the milk as it effects the rate of proteolysis is discussed. It is emphasized that this effect is of importance in using milk cultures to indicate proteolytic activity. The use of lactic organisms in cheese making and in the production of silage is accompanied with success. H. F. ZOLLER

The albuminoids of milk. M. BEAU. *Le lait* 1, 19–26(1921).—B. proposes a new classification of the protein constituents in milk: (1) "Lactein" for the total albuminoid matter as it exists in natural fresh milk; (2) "casein" for that which is produced in a coagulated condition by the effect of pressure or acids without heat (major part of which is alpha casein of Lindet and Ammann); (3) "albumin" for that produced by the effect of heat alone on milk after removal of the "casein" (and consists of beta casein of Lindet and Ammann together with traces of their alpha casein). The argument for the above classification is based upon the idea that too little attention is paid to the complex colloidal constituents of milk in their analytical sepn. [It is not evident that such a classification is necessary here in the U. S.—ABSTR.]. H. F. ZOLLER

What is a fair standard for ice cream? R. M. WASHBURN. *J. Dairy Sci.* 4, 231–9(1921).—The multitude of state and local standards are compared and discussed. Present standards are based on some standard for cream instead of on the needs of ice cream as a food. The nutritive ratio (muscle-producing to heat-producing components) of ice cream is much higher than milk and much higher than is necessary for a food consumed for its cooling effect in the summer. A fat content of 10% for vanilla and 8% for fruit, nut and chocolate creams are suggested as being sufficient for all purposes. H. A. LEPPER

Rotating thermocouple and cold junction for temperature studies in commercial ice-cream machines. HARPER F. ZOLLER. U. S. Dept. Agr. *Ice Cream Trade J.* 17, No. 8, 40–43(1921).—A multiple-junction, copper-constantan thermocouple is described

which has been adapted to the moving shaft of a factory ice-cream machine. Its special features are two: (1) insulated cold junction surrounding the reference bulb and affixed to the same shaft which carries the temp.-measuring bulb dipping into the ice-cream mix; (2) method of conducting the potential lead wires from the swiftly rotating shaft to the potentiometric system. The last is accomplished by means of two ring commutators of Cu with sharp edges mounted on the horizontal shaft and dipping into the pools of Hg. The Hg rapidly wets the Cu discs and hence thermoelec. friction is very small at these points of contact. The thermocouple described has 5 junctions and develops a p. d. of 201 microvolts per degree C. change in temp. in the region about 0°. Cross-sectional view of the construction is given as well as a photograph of the actual set-up. H. F. ZOLLER

Two organisms of a commercial lactic starter. S. HENRY AYERS AND COURTLAND S. MUDGE. *J. Dairy Sci.* **4**, 240–9(1921).—Two cultures of streptococci which seemed to be necessary to reproduce the original acidity and flavor were isolated from a com. starter. One culture was evidently a strain of the *Streptococcus lacticus* group and the other appeared to be of the *Streptococcus kefir* type. The former produced high acidity and little volatile acid in milk and the latter produced little total acidity in milk but considerable volatile acid in *Streptococcus lacticus* culture. Associative action between the two cultures was very noticeable. Exptl. work is given and cultural characteristics of the organisms are described. H. A. LEPPER

Use of aluminium sheeting in wrapping cheese for trade. K. TEICHERT AND H. PAULI. *Jahrb. Milchwirtschaft* **1**, 102–108(1921).—Because of the action of salts of Na and NH_4 upon the thin metal sheet it is rapidly destroyed in many instances. Likewise owing to the impurities often present in Al, galvanic couples are frequently formed and such Al is subject to deterioration. Its use in the industry is discouraged. H. F. Z.

Investigations of the composition of cheese curd and pressed and salted cheese. E. HOGLUND. Kgl. Landtbruks. *Akad. Handl. Tid.* **60**, 103–117(1921).—The investigations confirm the result of former work that the % of fat in the dry matter of the pressed and ripened cheese can be accurately calcd. on the basis of the % of fat in the dry matter used in making the cheese, the added salt being considered. Besides the present investigation has shown that the % of fat in the dry matter of the cheese curd must be detd. before the whey automatically seps. from the sample if the results shall be used as a basis for calcg. the compn. of the salable cheese. The sepn. of the whey increases the content of dry matter and decreases the content of fat. This sepn. of the whey in the sample has greater influence on the content of fat in the sample than the whey which is removed in pressing the cheese. C. O. SWANSON

Cheese making from pasteurized milk. L. FR. ROSENGREN. *Kgl. Landtbruks-Akad. Handl. Tid.* **60**, 203–218(1921).—The greatest practical value of pasteurizing milk in cheese making is to insure the quality of the cheese. This is especially true when milk is used from several sources where production and handling of the milk are not done under control of the cheese maker. If milk has a high degree of acidity, the pasteurization, preferably in connection with neutralization, is a condition for successful cheese. The neutralization must be done immediately before pasteurization. Short-time pasteurization gave as good results as long time. C. O. SWANSON

Approximate determination of margarine containing sesame oil in butter by means of the Baudouin reaction. ERNST JOSEF KRAUS Aussig a. E. *Z. Nahr. Genussm.* **41**, 178–9(1921).—When butter is adulterated with margarines with known sesame-oil content (10% was the rule in Germany) the following adaptation of Baudouin's reaction is useful in detg. the approx. amt. of margarine present in a butter. Three-g. samples of butter-margarine mixts. freed from H_2O and albuminous compounds were placed in 30-cc. glass-stoppered cylinders Twenty cc. concd. HCl and 0.3 cc. 2% alc. furfural

soln. were added and the mixts. shaken. The colors developed were compared with a standard color prepared by adding sesame oil to a similar fat mixt. L. D. ELLIOTT

Peculiar types of lard. J. ANGERHAUSEN. Hamburg. *Z. Nahr. Genussm.* **41**, 73–5(1921).—Several lards from Holland possessed a yellowish creamy color, were permeated with small grayish particles and had a stale, oily or tallowy taste. 'An analysis of 2 typical samples showed a low acidity in connection with a positive Kreis rancidity test. The Halphen and Bellier tests were positive but phytosterol was absent. All the common constants showed values within the range of lard. The proportion of hard fat crystg. from acetone amounted to 16–18%. The absence of vegetable fat was indicated by the absence of phytosterol. A. concludes the samples are pure lard refined from rancid lards, the presence of aldehydes remaining after refining giving rise to the positive Kreis test as well as the Halphen and Bellier test. L. D. ELLIOTT

Experiments in preserving eggs in Italy. M. PASSERINI. *Boll. soc. ital. Studio dell'alimentazione* **1**, 23–30(1919); *Bull. Agr. Intelligence* **11**, 263.—Eggs, taken fresh, washed, lightly rubbed with lard contg. 1% salicylic acid can be preserved over 7 mo. in a cool dry place. Loss in wt. (H_2O), 5% in 231 days, was reduced to 3% by wrapping each egg in oiled paper. Immersion in lime water kept eggs 14 mo. The slight lye taste developed in eggs so kept is probably due to impurities of the CaO, as it does not develop in sufficiently pure lime water. Liquefaction of the albumin is not believed by P. to be due to passage of $Ca(OH)_2$ into the egg, as this occurs with dry preserving and is probably a mol. change in the albumin as well as a hydrolysis. Partial sterilization at 60° before immersion in lime water did not give good results and before dry preserving in closed vessels, fat coated or not, gave disastrous results. The same results followed when eggs were exposed to Et_2O vapor. H. A. LEPPER

Example of the chemical analysis of honey. Chemical analysis of honey from Friuli near Udine. E. PERRONCITO AND GIOVANNI ISSOGLIO. *Ann. accad. agr. Torino* **62**, 152–3(1919).—D_{15} after diln. 1:2, 1.1212; apparent d_{15} 1:2, 1.3636; total acidity as formic acid, 0.07%; H_2O, 17.30%; ash, 0.45%; invert sugar, 73.55%; dextrose, 36.40%; levulose, 37.15%; sucrose, 4.27%; non-sugar, 4.88%; N. 0.12%; rotatory power $[\alpha]_D^{20}$, 2.8; Lund reaction, 1.8 cc. ALBERT R. MERZ

Inulin and its derivatives. DANIEL. *J. fabr. sucre* **62**, No. 29(1921).—It is proposed to use chicory for the large-scale production of levulose and a brown food color known by the trade name of "kulex" which is somewhat similar to caramel but may be prepd. in a dry powdered form. L. E. GILSON

The microscopical investigation of coffee substitutes. (Narcissus bulbs, an emetic raw material; sea grass). C. GRIEBEL AND W. ROTHE. Berlin. *Z. Nahr. Genussm.* **41**, 69–73(1921).—A few coffee substitutes were found to contain ground narcissus bulbs whose emetic action is not destroyed by roasting as in the case of sea grass (*Zostera marina* L.), which is a common and valueless substitute. L. D. ELLIOTT

Contributions to the investigation and valuation of chicory and other coffee substitutes. J. PRITZKER AND R. JUNGKUNZ. Basel. *Z. Nahr. Genussm.* **41**, 145–69 (1921).—A more extensive analysis of coffee substitutes as a basis of judgment is urged. An indirect method for the detn. of the ext. in chicory and other substitutes gave close agreements with results obtained by the direct method of weighing. Ten g. of sample are covered with 200 cc. distd. H_2O in a 400-cc. flask and the total wt. is recorded. After agitating and boiling for 5 min. H_2O is added to bring back to the original wt.; the suspension is mixed well and filtered. The d_{15} of the filtrate is obtained and the corresponding % read off on an appended table worked out by the authors, or calcd. by the following formula: $E=(S-1)\times 5160$, in which E = ext. per 100 g. substance, S = sp. gr. of the 5% ext. While the ext. in pure coffee is usually near 25% in a large number of substitutes analyzed the ext. rarely ran below 50%. The so-called "richness" (Ausgiebigkeit)

of the different substitutes is identical with the color intensity of the ext. but, among the different substitutes, is not always proportional to the strength of ext. The acidities of the different exts. varied from 8 to 46 cc. *N* alkali per 100 g. substance compared with 12 cc. for the 4 samples of pure coffees analyzed. The sand-free ashes of 38 samples of chicory were analyzed and the values compared with those obtained by other workers. The ash of chicory has a noticeable excess of alkalinity. Tables are given showing analyses of 38 chicory coffees and 18 other substitutes. L. D. ELLIOTT

Ground cinnamon adulterated with ocher, including a contribution to the ash and sand content of insect powder. RICHARD WINDISCH. Keszthely (Hungary). *Z. Nahr. Genussm.* **41**, 78–81(1921).—Samples of ground cinnamon contg. an excessive amt. of reddish ash were first suspected of being adulterated with hematite but investigation convinced W. that ocher had been added. Results for the ash of 5 com. insect powders are given. L. D. ELLIOTT

Determination of the volume of the insoluble part of marmalades, vegetables, fruits, chocolate, etc. A. HANAK. Brünn. *Z. Nahr. Genussm.* **41**, 179–80(1921).—For exact detns. the vol. of the insol. portion is detd. as follows: the sp. gr. of a suspension of the material (20 g. material per 100 cc. suspension) is carefully detd. in a 50-cc. pycnometer. A second similar suspension is filtered and the sp. gr. of the filtrate detd. in the same way. The insol. material on the filter is dried at 105° and weighed. The vol. sought is obtained by the formula: $x = 10\ (G - b + a)/s$ in which G is the wt. of insol. portion in 10 g. of marmalade or other material, b the wt. of the 50 cc. of suspension of 10 g. of material, a the wt. of the 50 cc. of filtrate and s the sp. gr. of the filtrate. L. D. E.

Boletus edulis conserves. JOS. GERUM. Erlangen. *Z. Nahr. Genussm.* **41**, 123–6(1921).—It was found that there was considerable loss of protein when the liquor on mushroom conserves, made from *Boletus edulis*, was poured off and they were cooked in fresh brine. D. B. DILL

The analysis of soup flavoring preparations. JÁR. BULÍR. *Chem. Listy* **15**, 132–8 (1921).—The soup flavoring exts. are prepared industrially by hydrolysis of various protein substances (casein, lactalbumin, aleuronates, horny material, etc.) with concd. HCl. The resulting product is neutralized with Na_2CO_3, filtered and concd. to the proper consistency. Various press cakes, leguminates and other vegetable materials, contg. considerable quantities of carbohydrates, are sometimes used as substitutes for the more nitrogenous substances. A chem. method for the detection of these substitutes was sought. The more nitrogeneous substances on hydrolysis yield small amts. of levulinic acid. A large amt. indicates the presence of substances rich in carbohydrates. B., therefore, proposes the following quant. method for the detn. of levulinic acid by means of β-naphthylhydrazone: 20 g. of the ext., neutralized if necessary, are evapd. to dryness on a water bath in a suitable porcelain dish. One g. of powdered tartaric acid is added and the mass triturated with a sufficient amt. of anhydrous Na_2SO_4 (80–100 g.) so that a dry, loose mixt. results. This is then transferred to a 200-cc. glass-stoppered flask, 100 cc. of ether are added with a pipet and the whole is allowed to stand for 24 hrs. with occasional stirring. 50 cc. of the clear ether soln. are taken and evapd. to dryness. The residue is dissolved in a small amt. of cold water and filtered into a small porcelain dish. In order to det. the amt. of β-naphthylhydrazine that is to be used for the pptn., this aq. soln. is titrated with *N* NaOH, phenolphthalein being used as an indicator. The amt. of *N* NaOH used in cc., multiplied by 0.1161, expresses the acidity in terms of levulinic acid. This neutralized soln. is evapd. to dryness and the residue is dissolved in 2 cc. of water, filtered if necessary, and transferred to a drying bottle. Four portions of water, 2 cc. each, are used for washing the dish, all of the wash water being added to the main soln. If the acidity, as detd. above, is equiv. to less than 0.06 g. of levulinic acid, the soln. has to be concd. to 5 cc. To this are added 2 drops of dil. AcOH and

1½ times the theoretical amt. of β-naphthylhydrazine-HCl, *i. e.*, for each part of levulinic acid present, 2.5 pts. of a 1% soln. of the reagent are added. The stoppered drying bottle is allowed to stand at room temp. for 4 hrs. The pptd. β-naphthylhydrazone is filtered onto a Gooch, washed with four 15-cc. portions of cold water, dried for 3 hrs. at 85–90° and weighed. The wt. multiplied by 0.453 gives the wt. of levulinic acid to which is added 2 mg., the amt. sol. in 60 cc. of wash water, and 0.35 mg. $\times (V/10)$, where V is the vol. of the soln. in which the pptn. takes place. The same procedure is followed in the detn. of levulinic acid in bouillon cubes, pastes, etc. The amts. of levulinic acid, expressed as % in org. dry substance, present in exts. prepd. from various sources, are as follows: crude casein 0.20%; crude lactalbumin 1.20%; horny substance none; aleuronate 2.02%; extd. grain germs 4.77%; rape press cake 7.60%; poppy press cake 6.16%; lupine (without the bitter principle) 13.77%. JOHN M. KRNO

Fermentations which occur in making silage. CHR. BARTHEL. *Kgl. Landtbruks-Akad. Handl. Tid.* 60, 92–102(1921).—In an address before the Royal Agr. Acad. B. gives first a general statement of the principles which govern the processes of making good silage. B. and co-workers detd. lactic acid, volatile acids, total acids, H-ion concns., total N, N in peptones and amino acids and N as NH_3 in various kinds of silage. Butyric, propionic and acetic acids were the volatile acids found. The av. p_H was 3.7 in good silage. A very poor grade of silage from a pit silo had p_H of 4.55. In the best silage the acids are principally lactic and acetic. The presence of butyric acid is indicative of putrefactive fermentation. In good silage the amt. of N in peptones and amino acids varied from 22.8 to 45.3% of the total. Poor silage had the largest % of N in the form of NH_3. The loss of org. matter should not exceed, under favorable conditions, 20% of the total dry matter. C. O. SWANSON

The manufacture of starch, glucose and by-products (WILLIAMS) **28.** The relation of protein content to variety types in American wheat (ROBERTS) **11D.** The utilization of the carnauba-wax palm (GRIMME) **27.** A lactic ferment very frequent in milk (VIOLLE) **11C.** Meat production (MURRAY) **11E.** Sterilizing with nitrogen trichloride (U. S. pat. 1,378,644) **14.**

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Apparatus for treating milk or other liquids with ozone. F. N. BEYER and J. H. LOUNGE. U. S. 1,378,314, May 17.

Apparatus for pasteurizing bottled milk, etc. K. K. WRIGHT. U. S. 1,377,742, May 10.

Apparatus for cooking or sterilizing corn or other foods. W. B. [illegible]. U. S. 1,377,245, May 10.

Dehydrating potatoes. A. E. ALLEN. U. S. 1,377,172, May 10. Potatoes are

cooked until soft, formed into filaments, dried at a temp. below 70°, broken into short sections and then dried at a temp. above 70° for a short time.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The technical and ethical relations between different forms of the same invention. OTTO OHNESORGE. Bochum. *Brennstoff Chem.* **2**, 177–81(1921).—A discussion of certain aspects of the German patent law relative to "partial identity" in inventions. W. B. V.

The German chemical industry since the war. J. SINGER. *Chem. Weekblad* **18**, 7–9(1921).—A brief review of the financial condition of the various German chem. companies in 1919. L. H. ADAMS

Report of the committee on occupational diseases in the chemical trades. CHARLES BASKERVILLE, Chairman. *J. Ind. Eng. Chem.* **13**, 568–9(1921); cf. *C. A.* **14**, 2230.—Improved conditions with respect to occupational diseases are due partly to the installation of equipment and partly to decrease in chem. production. Methanol is less attractive under this name. Gas masks of special character are being used. The gases themselves are often beneficial, the employees in SO_2, Cl, Br, H_2S, $COCl_2$ and chloropicrin production being especially immune to disease. The Chairman suggests that a member of the U. S. P. H. Service could best continue the work. H. C. HAMILTON

Problems of lubrication. W. B. HARDY. *Proc. Roy. Inst. Gt. Britain* Feb. 27, 1920, 8 pp.—Resistance to motion is not always least when two solid surfaces are completely floated apart. For a glass bottle sliding down an ordinary glass plate stops when it strikes a portion of the glass wetted with water, so that water here acts as an anti-lubricant (cf. *C. A.* **14**, 1475). The glass is covered with a thin layer of grease. If this is removed the water acts no longer as an anti-lubricant but is merely neutral. Other neutral substances are alcohol, benzene, and strong ammonia. Lubricants do not necessarily have a high viscosity and substances having a high viscosity like glycerol, may facilitate slipping only when the surfaces are floated apart. Acetic acid and tripropylamine, on the other hand, have low viscosity and are admirable lubricants. Water and alcohol as well as every liquid tried act as lubricants for clean surfaces of bismuth. This leads to the view that lubrication is due to chemical action. The relation between lubricating power and chem. constitution was investigated by measuring the force required to move a slider of Bi over a surface of the metal. The static friction in simple chem. series such as the fatty acids, alcohols, and paraffins, decreases with the mol. wt. but not in a simple manner, chem. constitution playing an important part. At the point in the series where the lubricant becomes a solid at the temp. of observation there is no break. The more satd. cyclic compds. are better lubricants than the less satd. cyclic compds., but no ring compd. is a good lubricant. Esters are inferior as lubricants to their related free acids and alcohols, but to this rule the ring esters are exceptions. The hydroxy acids have remarkably high lubricating power, but the ring compds. are again exceptional. The friction of two clean surfaces is not due to inequalities of the surfaces, for plate glass and ordinary glass show the same friction; but it is due to adhesion between them. The function of the lubricant is to diminish the capacity for seizing by satg. the surface forces of the solid. A film of oxide or sulfide on a surface of copper acts as a very effective lubricant, owing to the lowering of the surface energy. EUGENE C. BINGHAM

Report of the Lubricants and Lubrication Inquiry Committee. *Dept. of Scientific and Industrial Research, Advisory Council. H. M. Stationery Office* **1920**, 126 pp. S. DONKIN, Chairman.—Tests of mineral oils with a Lanchester worm gear show that a critical

temp. is reached at which the running of the gear becomes unsteady. With animal and vegetable oils no critical stage is reached below 75°. Castor oil gives the highest efficiency (95.6%); then come rape and trotter oils (95%). Sperm oil shows a gradual decrease in efficiency as the temp. rises. On adding 2.5% rape oil to mineral oil the critical temp. is raised, but further addition of rape oil is without effect. Colloidal graphite is slightly beneficial. At pressures obtaining in the gear, the viscosity of castor oil is 6 times that of trotter oil at the same temp. so that the efficiency (the same for both oils) is not dependent upon the viscosity alone. The viscosity increases very greatly at high pressures. On increasing the pressure to 6.5 tons per sq. in. the viscosity of one mineral oil increased 25-fold, whereas that of castor oil and trotter oil increased 4-fold. The general conclusion is reached that mineral oils are more susceptible to the effects of high pressure than are fatty oils. In order to obtain a possible correlation between "oiliness" and other physical properties, sp. gr., viscosity, surface tension, thermal cond., and dielec. const. were studied, but without positive result. The report reviews existing knowledge of lubrication and suggests several lines along which research is needed. The following appendices are a part of the report. **Internal friction of liquids under high pressure.** O. FAUST. (Cf. *C. A.* 8, 1373). **The determination of the compressibility of lubricating oils under high pressures, and the application of the results to the tests in the high-pressure viscosimeter to obtain the values of the viscosities of the oils.** J. H. HYDE. The values of the compressibilities of the oils were found to differ very little from each other and from that of water. On the other hand, in Mobiloil "BB" a pressure of 1000 kg. per sq. cm. (6.47 tons per sq. in.) increases the viscosity 26.45-fold, whereas in fatty oils the same pressure causes an increase in viscosity of only about 4-fold. **The determination of certain physical properties of the oils used in the Lanchester worm gear experiments.** ANON. The surface tensions of the fatty and mineral oils vary only between narrow limits at 12° (from 34.3 dynes per sq. cm. for Mobiloil "A" to 38.5 for Victory Red Oil). Glycerol and other non-lubricating oils have a much higher surface tension. The sp. heats vary from 0.423 c. g. s. units for Victory Red oil to 0.508 for castor oil. Fixed oils have a uniformly higher sp. heat than the mineral oils tested. Glycerol has a still higher sp. heat. The dielec. const. varies from 2.25 for "FFF" cylinder oil to 4.64 for castor oil. The fixed oils have uniformly higher dielec. consts. than the mineral oils. Non-lubricating oils have a high dielec. const. **Testing the viscosity of oil at high pressure.** CHARLES A. PARSONS. A design is given of an app. having two cylindrical surfaces arranged concentrically so that the oil film between them would be subjected to the same shearing speed and have the same thickness as in steam turbines. **Variation in the efficiency of a worm gear due to differences in the lubricant employed.** J. H. HYDE. Data are given for 7 oils; the mean load on the teeth was 1.5 and 2.0 tons per sq. in. and the speed was 1080 and 1500 r. p. m. Small additions of rape oil to mineral oil raise the temp. at which a possibly serious falling off in lubricating value of the latter begins to occur. **An apparatus for the determination of the absolute viscosities of liquids at high pressures and the results obtained with it for certain lubricating oils.** J. H. HYDE. The app. consists essentially of a system of two horizontal and two vertical tubes, forming a closed circuit under pressure. The upper tube is of capillary dimensions; it is filled with the liquid under test; the lower half of the circuit is filled with mercury. Displacement of the mercury causes flow around the circuit. By having one end of the system resting on a horizontal knife edge and the other supported by a small spring, it is possible to maintain the rate of extension of the spring just equal to the change in head of the mercury, so that the flow takes place under a const. pressure head and at a velocity which can be calcd. from the extension of the spring. Castor oil, trotter oil, Mobiloil "BB," Mobiloil "A" and Bayonne oil all showed a rapid increase in kinematic viscosity with the pressure but the

increase was far greater for the mineral oils than for the animal or vegetable oils. **Apparatus for the examination of the viscosity of oils under any pressure.** C. V. BOYS. Similar to the preceding in general purpose but worked out differently. **Description of oil-testing apparatus designed by R. M. Deeley.** ANON. Cf. *C. A.* **14**, 1475. **Précis of report by T. C. Thomsen on the cup-and-ball viscosimeter designed by Michell.** ANON. Errors of 50% may be obtained in the use of this app., due largely to lack of temp. control; hence the instrument should be immersed in a bath. **Report on tests made in the Lanchester worm gear testing machine on three samples of aircraft oils.** J. H. HYDE. With Mobiloil "A" the efficiency is practically const. at 95.5 up to about 50°, where it begins to fall off. Mobiloil "BB" gives a const. efficiency of 94.8 below 60° but falls off rapidly above that temp. The efficiency of castor oil falls very gradually from 96.1 at 35° to 95.4 at 100°. **Report on the characteristics of the flow of oil over a journal bearing.** J. H. HYDE. An attempt is made to demonstrate the flow of oil over a simple journal bearing. **Memorandum on J. H. Patterson's suggested method for preventing the separation of oil emulsions when mixed with salt water.** ANON. When salt was present in sufficient quantity (0.2%) to cause sepn., the addition of gelatin did not prevent the sepn. Glucose seemed to increase the sepn. **Results of examination of a sample of "Aliphol Omnium" compounding medium for lubricating oils.** ANON. **Trials of "Oildag" in aero engines by the Air Ministry.** D. R. PYE. The tests indicate that the use of "Oildag" may lead to reduced oil and gasoline consumption but increased carbonization. **Determination of the frictional coefficient of shaft bearings (plummer blocks) using a lubricant with and without the addition of "Oildag."** J. H. HYDE. Bayonne oil shows a reduction in the coeff. of friction of 11% when "Oildag" is added.

EUGENE C. BINGHAM

The improvement of the lubricating properties of mineral oils. J. H. HYDE. *Engineering* **111**, 708–9(1921).—Tests made on the Deeley friction testing machine (cf. preceding abstract) and the Lanchester worm gear machine (cf. *C. A.* **14**, 1475) prove that, on adding oleic and other organic acids to a mineral oil, a very considerable reduction in the static friction is produced. So little as 0.1% of fatty acid effects a very considerable reduction, oleic acid, acid rape oil and the rape oil fatty acids all having similar effect. The Lanchester machine shows a gear efficiency of 96.0% with straight mineral oil; on adding 0.2% of oleic acid the efficiency is raised to 96.4%.

EUGENE C. BINGHAM

Insulators from synthetic resins and asbestos. ANON. *Neueste Erfind. u. Erfah.* **47**, 14–8(1920); *Chimie & industrie* **5**, 73(1921).—Review of the properties and uses of bakelite A, B, C, and especially of the prepn. of elec. insulators from bakelite mixed with 60–70% of asbestos. A. P.-C.

The technic of low temperatures. ANON. *Wärme u. Kalte Technik* **22**, 169–72 (1920); *Chimie & industrie* **5**, 177(1921).—Historical sketch of the methods used for obtaining low temps. and liquefying gases, and more particularly air. After describing the sepn. of O_2 and N_2 by the Linde process, the author discusses the utilization of the two gases. A. P.-C.

A comparative study of fractionating still-heads (MOORE) **1**. Application and use of immersion electric heaters (STRAIT) **1**. Mill for colloidal comminution in industrial chemical work (NASKE) **1**. Gas flow measurement (LAMBERT) **21**.

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Distilling waste grease. L. LANE and D. H. WILLIAMS. Brit. 163,056, June 5, 1920. Waste roll or axle grease or pitch obtained from steel-works, tin-plate rolling-mills, etc., is distd. to obtain oils and greases, and, in some cases, a residue, of coke. The waste grease is melted in a primary still from which the vapors are led by a pipe to a condenser. The melted grease is drawn off by a perforated pipe to a main still. The vapors pass to a condenser in which, by means of cocks, alternative passages may be opened. The light vapors are passed through pipes and a coil immersed in a cooling tank. The middle vapors are passed through pipes and into the cooling-tank and the heavy vapors through other pipes. A tank containing a freezing mixt. may be used to condense very light vapors. Air may be injected into a pipe to assist in condensing the heavy vapors. Stirrers are provided in the stills. The liquid residue from the still may be distd. in a sep. still to form coke.

Purifying liquids by filtration. J. P. PROBST. U. S. 1,378,274, May 17. Mechanical features.

Mixing gases. F. A. STAMPS. U. S. 1,378,429, May 17. The pat. relates to the regulation of velocity of flow of different gases through supply pipes so that they will be supplied to a mixing chamber in a fixed ratio of relative quantities.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

A suggestion on a method for purifying water and its significance in laboratory practice and sanitary water analysis. G. A. LINHART. Berkeley, Calif. *Leaflet*, 2 pp (1919).—The principle that a solvent may be completely sepd. from a solute by freezing may be used in treating alkali water for use for irrigation purposes. Tap water which was frozen in the usual way with air agitation resulted in the concn. of all mineral salts into a core which was 6% to 8% of the total wt. of the cake. The concn. ratio for Cl and NO_3 was 12.5 and 12.4, resp., Cl^-, NO_3^-, SO_4^{--} NO_2^- and NH_4^+ were absent in the clear ice. Conclusions: (1) Freezing offers a simple and accurate method of concg. extremely dil. solns. for chem. analyses (cf. Le Roy, *C. A.* **10**, 1564). (2) Freezing the core as ordinarily done in ice manuf. represents an enormous waste of energy. Core water should be pumped out and the cake left hollow or the space could be filled with melted ice and frozen solid. (3) Theoretically and in practice much more energy is required to vaporize than to freeze water. Water from clear ice could be profitably substituted for distd. water used in chem. labs. (4) Ice cores even though they contain no visible dirt may constitute a health menace. W. F. LANGELIER

Alterations to Queen Lane Water Filters, Philadelphia. JOHN S. ELY. *Eng.*

News Record **86,** 942–3(1921).—The filter plant consists of 22 slow sand filters of 0.75 acres each, 40 preliminary filters (each 32×40′), a 40,000,000 gal. filtered water basin, and appurtenances. It is proposed to convert the 40 preliminary filters into rapid sand filters with a capacity of 100 million gal. per day. The slow sand filters have a capacity of 40 m. g. d. giving a total of 140 m. g. d. as against 70 m. g. d. the present capacity. It is planned to construct 2 new settling basins 300 ft. long and varying in width from 64 to 80 ft. according to the width of bank on which they are built. Their depth varies inversely as the width. A mean velocity of 0.04 ft. per sec. and a settling period of about 2 hrs. is provided when treating 100 m. g. d. in both basins. FRANK BACHMANN

Coagulation of water with alum by prolonged agitation. WILFRED F. LANGELIER. *Eng. News-Record* **86,** 924–8(1921).—Expts. on the coagulation of the Sacramento River water indicated that with mechanical agitation from 0.5 to 0.8 gr. per gal. alum was required for flocculation. A turbidity increasing from 20 to 200 p. p .m. did not affect the speed of coagulation, and only a slightly larger dose of alum was necessary with the more turbid water. High alkalinities required longer agitation or an increase in dosage. Higher velocities speed up the flocculation and agitation gradually reduced gave better results than agitation followed quickly by quiescence. Velocities in the sedimentation basin should vary from 0.15′ per sec. at inlet to 0.02′ at outlet. Observations indicate that sedimentation is independent of depth of basin but is a function of the floor area. FRANK BACHMANN

Rate of solution of sulfate of aluminium. J. W. ELLMS, A. G. LEVY AND L. A. MARSHALL. *J. Am. Water Works Assoc.* **8,** 426–32(1921); *Eng. News-Record* **86,** 1039–40 (1921).—Given a 2½–10-inch vertical rise per min. the time of soln. is a factor of temp. only and with each 1° rise in temp. the time of soln. will decrease approx. 5%. Also in *Eng. Contr.* **56,** 136–7(1921); *Can. Eng.* **41,** Aug. 25(1921). D. K. FRENCH

Operation of the water-purification plants at Evanston, Ill. and Whiting, Ind. SAMUEL A. GREELY. *J. Am. Water Works Assoc.* **8,** 442–7(1921).—In the Evanston plant coagulation and sedimentation are sufficient. 0.7 gr. per gal. alum is used. At East Chicago the alum dose is about 2.0 gr. per. gal. At Whiting lime also is used and aeration in addition because of oil odors which must be removed. Aeration precedes coagulation. D. K. FRENCH

Tastes and odors from chlorination. WALTER A. SPERRY AND LLOYD C. BILLINGS. *Eng. News-Record* **86,** 1041(1921).—Owing to large quantities of org. matter in the water supplied Grand Rapids comparatively large doses of Cl are necessary. Studies with the Cl absorption has shown that the range between the amt. for disinfection and the amt. to give taste is small. Tastes as applied to filter plants are believed to be due to improperly proportioned dosages. FRANK BACHMANN

Boiler feed water and modern methods of purification. E. J. TOBI. *Chem. Weekblad* **18,** 311–7(1921).—A general discussion, in which boiler feed water, its chemical and thermal purification, and degassing are considered. References are given. NATHAN VAN PATTEN

State versus local viewpoint on filter-plant control. ROBERT B. MORSE. *Eng. News-Record* **86,** 1041–2(1921).—M. points out the necessity of coöperation and understanding between state officials and plant operators. Also in *Eng. Contr.* **56,** 138 (1921). FRANK BACHMANN

Application of colloid chemistry to sludge pressing. JOHN ARTHUR WILSON, WM. R. COPELAND AND HENRY M. HEISIG. *Eng. News-Record* **86,** 1042(1921).—By adding H_2SO_4 to the activated sludge at Milwaukee to give the sludge its optimum active acidity (H-ion concn.) the rate of filter pressing can be increased by 400%. By the addition of Cr or Al sulfate and acid to the optimum acidity, the rate of pressing was increased 900%. , *J. Am. Water Works Assoc.* **8,** 486–96(1921). FRANK BACHMANN

Air-lift removal of sludge from sewage tanks. W. G. KIRCHOFFER. *Eng. News-Record* **86**, 953(1921).—By installing air lifts for removal of sludge from settling compartments of the Madison, Wis., sewage tanks better efficiencies were recorded than with gravity removal of sludge to the digestion tanks. FRANK BACHMANN

Findings of Los Angeles sewage Disposal Commission. GEORGE W. FULLER, GEORGE C. WHIPPLE, AND WILLIAM MULHOLLAND. *Eng. News-Record* **86**, 1117–8(1921).—The Los Angeles sewage is strong with about 55 gal. per capita from those connected to the sewers. It contains 198 lbs. of suspended matter, 24 lbs. of N, 70 lbs. grease, and 6.5 lbs. of mineral oils per 1000 population per day. The commission favored screening the sewage at present and dispersing it into the ocean through deep multiple outlets. Expts. on the activated sludge process in a plant to handle 2.5 m. g. d. is recommended. FRANK BACHMANN

Providence resumes chemical precipitation. ANON. *Eng. News-Record* 953(1921).—Chem. pptn. of sewage with CaO was resumed the latter part of A[illegible]. Owing to lack of CaO and towage for sea dumping of sludge, chlorination only was practiced during the war. FRANK BACHMANN

Disposal of industrial wastes and stream pollution. C. A. EMERSON, JR. Penn. Dept. Health. *J. Franklin Inst.* **191**, 807–18(1921).—A discussion of the methods used for the prevention of stream pollution by wastes from tanning, wool scouring, gas, by-product coke, oil, iron and coal industries. JOSEPH S. HEPBURN

Sewage disposal for the isolated dwelling and small institution. R. B. WILEY. Purdue Univ. Eng. Exp. Sta., *Bull.* **6**, 36 pp.(1920); *Expt. Sta. Record* **44**, 383–4.—Sewage disposal should be so planned that it will not create a nuisance nor contaminate a water supply used for drinking purposes. Tank and aeration as methods of treatment are described and discussed. The location of the plant depends upon local conditions, but it should be placed on a side hill wherever possible and so located that the ground does not slope from the plant to any buildings, well, or springs. Details of construction are given. M. C. PERRY

The sewage irrigation field of the city of Dülman (KREUTZ) **15.** Determination of formaldehyde (KOLLO, LASCAR) **7.** Detection of fluorescein (LOMBARD) **7.** Determining the alkalinity in hypochlorite solutions (WESENER, TELLER) **7.**

JAMESON, W. WILSON and MARCHANT, F. T.: **Hygiene.** Philadelphia: P. Blakiston's Sons Co. 400 pp. $4.00 net. For review see *Am. J. Pub. Health* **11**, 753(1921).

SPITTA, O.: **Die Untersuchung und Beurteilung des Wassers und des Abwassers.** Berlin: Jul. Springer. M 96.

Preventing incrustation in steam boilers. A. PESSI. Brit. 163,013, May 6, 1921. Pyroligneous acid with or without alkali acetates and arsenites is used to prevent boiler incrustation. Suitable mixts. in aq. soln. comprize 20–40% of crude pyroligneous acid, 10–30% of soda and 0.5–1.5% of As_2O_3 or 3–6% of acetates or pyrolignites of alkali or alk. earths, 10–30% of soda and 0.5–1.5% of As_2O_3.

Apparatus for removing precipitated solids from boiler feed water. W. E. WINE. U. S. 1,377,996, May 10.

Electrical purification of sewage and the like. C. P. LANDRETH. U. S. 1,378,120, May 17. Sewage, tannery effluent and the like are purified by electrical treatment, With electrodes of Fe or steel together with sufficient reagent such as milk of lime to produce nascent O and induce passivity of the electrode.

Sterilizing with nitrogen trichloride. J. C. BAKER. U. S. 1,378,644, May 17. NCl_3 is used for sterilizing water, sewage, milk or other materials. In order to avoid

danger attending its use, it is generated as required by dissolving Cl in H_2O to the extent of 0.1% to 0.5% and passing this soln. through a mass of crushed limestone until all the Cl is converted to HOCl and the HCl is completely neutralized, and then bringing the soln. thus formed into admixt. with an aq. soln. of NH_4Cl, $(NH_4)_2SO_4$ or NH_4OH. In sterilizing water by this method, in some instances greater economy may be attained than with the use of Cl. In some instances with sewage a smaller quantity of NCl_3 than Cl will accomplish an equal sterilizing effect. *Fruits and other solid articles* may be sterilized by volatilizing the NCl_3 and bringing it into contact with the material.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER AND ALBERT R. MERZ

The genesis of a fertile soil. J. B. HARRISON AND C. B. W. ANDERSON. *West Indian Bull.* **18**, 77–98, No. 3(1920).—This paper presents extensive and very minute chemical analyses of materials entering into the compn. of the Barbados soils. It is shown by a careful geological study that the origin, directly or indirectly, of these soils is the air-borne débris of the volcanoes of St. Vincent, and possibly of the Grenadines and other vents of the West Indian volcanic province. R. B. DEEMER

Soil acidity in its physico-chemical aspects. E. M. CROUTHER. *Trans. Faraday Soc.* **1921**, May 31 (adv. proof).—A discussion of the methods used in the detn. of soil acidity and of the action of neutral salts on acid soils and the relation of soil acidity to plant growth. RUSSELL M. JONES

The system: Soil—soil moisture. BERNARD A. KEEN. *Trans. Faraday Soc.* **1921**, May 31 (advance proof).—K. compares the original hypothesis of the relation between the soil and its moisture content to the modern one. Colloidal matter in the soil has a profound effect on moisture relations and extends over a wide range of moisture content. RUSSELL M. JONES

The physical properties of the soil in relation to survey work. G. W. ROBINSON. *Trans. Faraday Soc.* **1921**, May 31 (advance proof).—Defects exist in the present method of classifying soils. Mechanical analysis is of value in genetic classification of soils but should be supplemented by edaphic and cultural condition. A series of physical consts. to express this condition better is recommended. RUSSELL M. JONES

The part played by organic matter in the soil system. H. J. PAGE. *Trans. Faraday Soc.* **1921**, May 31 (advance proof).—An outline of the physico-chem. aspects of the relation of org. matter to soil fertility. The combined action of org. colloid and $CaCO_3$ regulates the texture of the soil, soil moisture, soil temp., and soil solns. so as to avoid harmful extremes of leaching and evapn. RUSSELL M. JONES

Osmotic phenomena. CHAS. A. SHULL. *Trans. Faraday Soc.* **1921**, May 31 (advance proof).—A discussion of osmotic phenomena with regards to osmotic pressure, cause of semipermeability of membranes, and of unilateral movement of water across the semipermeable septum. RUSSELL M. JONES

Application of physico-chemical methods to study of humus. SVEN ODÉN. *Trans. Faraday Society* **1921**, May 31 (advance proof).—Physico-chemical methods have been applied to the problem, namely, the acid or non-acid nature of substances occurring in humus. Expts. with suspension of pure humus acid showed the formation of humic ions, and the acid nature of humic acid. Acids forced out from humus by the addition of salts are probably partly of inorg. and partly of org. nature. These acids are poisonous to plant life while humic acids are relatively innocuous. Liming of peaty soil neutralizes toxic acid and forms lime humates which oppose formation of these acids. A vapor-tension curve for lime and unlimed humus is given. RUSSELL M. JONES

Phenomena of absorption in soils: a critical discussion of the hypotheses put

place. The mechanism of the changes is not set forth. Two colorimetric methods of *estg. phenol and cresols in soils* are original with S. 100 g. soil are placed in a round-bottomed liter flask and the phenol or cresol is steam distd. for a period of 2½ hrs., the distillate being collected in 500 cc. fractions at the end of 1, 2 and 2½ hr. intervals. The red color produced by Millon's reagent and concd. HNO_3 under standard conditions (not given) yields satisfactory results for any amt. down to 0.25 mg. of phenol, 35 cc. of the distillate being used. For smaller quantities the phenol is nitrated with cold H_2SO_4 and HNO_3; and neutralized with NH_4OH. The yellow color can be used for the estn. of as small an amt. of phenol as 0.01 mg. in 50 cc. of the distillate. The accuracy of this method is of a much lower order than that of the reaction with Millon's reagent. Both methods work equally well for cresols, but the conditions that produce the best color with Millon's reagent differ both among themselves and also from those in the case of phenol. R. B. DEEMER

Conservation of the soil. F. D. FARRELL. Kansas Agr. Expt. Sta., *Directors Rept.* **1918–19,** 14–27.—A report of soil fertility projects. Studies on the effect of fertilizers on yellowberry in wheat indicate that P and fertilizers reduce its percentage. In a study to det. the effect of prolonged production of alfalfa upon soil fertility, it is pointed out that in humid sections cropped soil contains ⅓ less N, and 36% less C than the soil in native sod. Alfalfa soil contains 23.8% more N and 18% more C than the cropped soil, but 13% less N and 21% less C than the native soil. In subhumid sections, cropped soil contains ¼ less N than native sod soil. Alfalfa soils contain 20% more N than cropped soil, but 5% less than native soil. In semiarid sections the cropped soil contains one-fifth less N than native sod soil. Alfalfa soil contains 15.7% more N than the virgin soil and 30% more than the cropped soil. The av. P content of cropped soil is lower than alfalfa on virgin soil. J. J. SKINNER

Soil solutions in relation to the plant. D. R. HOAGLAND. *Trans. Faraday Soc.* **1921,** May 31 (adv. proof).—Some of the general relations of soil to the plant are outlined. Availability of nutrients should be measured by the rate at which they are supplied to the root system, for availability as detd. by expt. on water ext. is not accurate. H. suggests the following soil research problems: The rate of soly., CO_2 production, and nitrification, and absorption of solutes by different plants. RUSSELL M. JONES

Deficiency of plant food calcium in soils. O. M. SHEDD. Kentucky Agr. Expt. Sta., *Ann. Rept.* **32,** 29–31(1919).—Six soils low in Ca were used in pot expts. to which Ca citrate, Ca oxalate, and a Ca-Na citrate were applied; they were checked against similar Mg compds. Soy beans, alfalfa, and sweet clover were grown. The response of Ca was more marked to vegetative growth than to seed production. The effect of Ca varied with the different soils. J. J. SKINNER

The retention of soluble phosphates in calcareous and non-calcareous soils. J. SEN. *Sci. Repts. Agr. Research Inst., Pusa* **1919–20,** 35–9.—The distribution of P_2O_5 in calcareous soils is less than in non-calcareous, owing to $CaCO_3$ fixing P_2O_5 in the upper soil layers. Available P_2O_5 is also less. P_2O_5 in non-calcareous soils is held by adsorption. H. W. EASTERWOOD

Nitrate production in a soil as affected by crop and cultivation. WM. A. ALBRECHT. Missouri Agr. Expt. Sta., *Bull.* **172,** 41(1921); cf. *C. A.* **14,** 2232.—Results of the past 2 years indicate that nitrates accumulate early in the season until the plant makes its max. growth. They remain low for the remainder of the season. Plowing has a significant effect toward increasing nitrates. Cultivation of the surface soil reduces the nitrates in the upper 7 in. of soil. The mulch has a depressing effect on nitrate accumulation. Significant reduction of nitrates follows continued rains on open soils. High concns. of nitrates were noticed in fallow soils. RUSSELL M. JONES

Supply of nitrogen in the soil. J. W. AMES. Ohio Agr. Expt. Sta., *Mo. Bull.* **5,**

174–7(1920).—A comparison of the N content of plots in the fertilizer expts. at Wooster is made. Soil cropped for 16 years with corn lost 867 lb., with oats 567, and with wheat 325 pounds of N per acre. The data show that depletion of the N supply is less when crop yields are increased by proper treatment of soils with fertilizers, manure and lime.
J. J. SKINNER

Agricultural chemistry. Investigations. Soil studies. ANON. North Dakota Agr. Expt. Sta., *Bull.* **136,** 18 pp.(1919).—Of a number of soils examd. which had been cropped differently there was a marked uniformity in the amt. of N at a depth of 18–24 inches, for P at a depth of 20–30 in., Mg at a depth of 6–12 in., Ca and CO_2 at a depth of 30–36 inches. The total Mg is in excess of Ca to a depth of 18–30 in. Water-sol. Mg. was greater than Ca in wheat soils beginning with the stratum 12–18 in. J. J. S.

Agricultural lime. M. F. MILLER AND H. H. KRUSEKOPF. Missouri Agr. Expt. Sta., *Bull.* **171,** 24 pp.(1920).—A general discussion of lime and its effects on crops. The limestones of Missouri are described and the analyses given of limestone in the various counties of the state. J. J. SKINNER

The alkaline reaction provoked by acids in soils with reference to plant nutrition. The rendering soluble of the phosphates in the soil. GIULIO MASONI. *Staz. sper. agrar. ital.* **53,** 121–3(1920); cf. *C. A.* **9,** 1816; **11,** 181.—The soly. of Fe, Al and Ca phosphates was studied as caused by org. and inorg. acids (*a*) when mixed with pure $CaCO_3$; (*b*) when mixed with calcareous soils; (*c*) in a mixt. of ordinary soil, $CaCO_3$ and mineral superphosphate. The quantity of acid used was in all cases insufficient completely to destroy the $CaCO_3$. The results indicate that phosphates behave similarly to Fe and Mn compds., greater quantities being dissolved by citric and malic acids. Oxalic acid showed a particular behavior with $Ca_3(PO_4)_2$ in that more P_2O_5 is dissolved by it in case (*a*) than by either citric or malic acids. ALBERT R. MERZ

Soil investigations. H. J. WEBBER. Calif. Agr. Expt. Sta., *Ann. Rept.* **1920,** 66–7.—Investigations on the fertilizer plots at Riverside, Calif., showed that fertilizing salts, except N, did not move below the surface foot. J. J. SKINNER

The value of "Tetraphosphate" as a fertilizer. J. HUDIG AND C. MEIJER. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* No. **25,** 140–64(1921).—"Tetra" is a remnant of the artificial fertilizers made to supply the great demand during and after the World War. It originated with Stoppani who, with the Thomas process in view, wanted to make insol. phosphates accessible to plants. By the Thomas-Gilchrist process in order to dephosphorize the iron in furnaces air is blown into the molten mass; the P is oxidized and is then taken up in lime. In this way a substance known as calcium tetraphosphate with the formula $Ca_3(PO_4)_2CaO$ is formed. Hoyerman found that if sand is added to this molten mass contg. the $Ca_3(PO_4)_2CaO$ a good fertilizer results. On Stoppani's researches an Italian company put out a fertilizer which was named "Tetraphosphate" (although it has no chem. or physical claim to the name). It was prepd. by fusing natural (insol.) phosphate with a mixt. of Na_2SO_4 and dolomite at 700° for ±3 hours and then cooling it in as much water as will just evap. during the cooling. The resulting "Tetraphosphate" (**A**) can not be distinguished physically nor chemically from a mixt. of insol. phosphate, Na_2SO_4 and dolomite. A claim was made that A is as good and in some cases even better than natural phosphate and almost up to the standard of superphosphate; this claim was upheld by the researches of Menozzi of Milan. The objec- of this research was then to find out whether A could be used profitably in the Nethert lands; accordingly A was tried in alk. as well as in acid media. Table 2 compares the yields of barley crops in both acid and alk. media with 8 different kinds of phosphate, including A. The mineral phosphates, including A, proved to be entire failures in alk. media while in acid media A was as good as any. Out of 59 exptl. plots phosphoric acid action could be detd. in 44 cases; out of these, 31 showed activity of A, and out of

these 31 cases, A activity was detd. in 9, where it was found to be far superior to the natural French phosphate, and at least as good as superphosphate. These results were obtained with grass, barley, peas, etc. Grain in general and potatoes do not give such favorable results; in 4 cases A gave even less favorable results than the natural phosphates. It is worth noting that A works better than the insol. phosphates in the case of such crops as the grasses and legumes (papilionaceous plants); in two tests made on potatoes in acid media (having very little P_2O_5) as well as in lime soils the results were very satisfactory, A working just as well as superphosphate and slightly better than the natural phosphates. A can thus only be used in slightly acid or acid soils and there the results are only slightly better than those obtained with finely ground up natural phosphates. A seems to have special advantages for such crops as grasses, peas, beans, etc. The good properties of A are apparently not due to the method of prepn. but to the presence of Na_2SO_4 and dolomite. Concluding, H. and M. suggest that the Dutch agriculture need not consider A as a new and desirable fertilizer with any advantages over superphosphate and that through this research it has become apparent that too little credit has been given natural phosphate in the past, since in many cases natural phosphate can be used to advantage in place of the more expensive superphosphate.

VINCENT VERMOOTEN

Phosphate fertilizers in the agriculture of the Argentine Republic. CAMILIO CIRANNA. *Anales soc. quim. Argentina* **8**, 31–40(1920).—The soils of Argentina are deficient in phosphates and are growing poorer owing to the large amts. of agricultural products exported. There is no domestic supply of phosphate fertilizers. Cf. following abstr. L. E. GILSON

A calculation of the quantity of phosphoric acid contained in the agricultural products exported from the Argentine Republic. PABLO LAVENIR. *Anales soc. quim. Argentina* **8**, 177–82(1920). L. E. G.

The presence of arsenic as a normal constituent of cultivated soils. F. REICHERT AND R. A. TRELLES. *Anales soc. quim. Argentina* **9**, 89–95(1921).—Twenty samples of soils from various parts of the Argentine Republic were analyzed. All contained As. The amts. found were from 1 mg. to 9 mg. As_2O_3 per kg. of soil. The arsenic is only partly extd. by H_2O but is completely extd. by dil. alk. solns. All the soils but one were very low in phosphates. L. E. GILSON

Determination of the relative values of different forms of phosphorus upon the soil at Columbia. M. F. MILLER, R. R. HUDELSON, AND F. L. DULEY. Missouri Agr. Expt. Sta., *Bull.* **172**, 38(1921).—Arranged in order of yield beginning with the highest, the different phosphates stand as follows: Calcined phosphate, acid phosphate, basic slag, rock phosphate, bone meal. RUSSELL M. JONES

Loss of water-soluble phosphate in certain fertilizer mixtures. ANON. *J. Dept. Agr. Union S. Africa* **2**, 552–3(1921).—Fertilizer mixts. contg. (1) high-grade superphosphate, (2) bone meal and (3) government guano were prepared and analyses made to det. the rate of and amt. of deterioration that takes place in the water-sol. phosphate. Results given indicate that the loss of water-sol. phosphate is not serious, especially if one takes into account the comparative availability of the resulting pptd. phosphates.

C. B. DURGIN

The determination of citrate-soluble phosphoric acid in superphosphate. ANON. *Chem. Ztg.* **45**, 487(1921).—The method as used by the association of German fertilizer manufacturers is outlined. Prepn. of soln.: Dissolve 173 g. of unweathered cryst. citric acid and 536.9 cc. ammonia (d. 0.96) in 1 l. of water. The soln. is analyzed for N. 2.5 cc. of the soln. should contain 0.1050 g. of N. Procedure: Grind 2.5 g. of superphosphate in a small mortar, first dry and then with the addition of 20–25 cc. of water. Decant the liquid and filter into a 250-cc. flask. Repeat the grinding with water 3

times. The sample should, by this time, be ground to a fine powder. Then place the residue on the filter and wash into the same flask till the total filtrate is 200 cc. If the filtrate is turbid clarify it with a few drops of H_2SO_4 or HCl. Then make the filtrate up to 250 cc. Transfer the filter paper and residue into a 250-cc. flask with a wide neck and shake with 100 cc. of Peterman's (citrate) soln. till the filter paper is completely disintegrated. Keep the flask stoppered till the end of the digestion which is continued either for 15 hours at room temp. followed by 1 hour on a steam bath at 40° or for 4 hours at 40°. Shake the flask about every 15 min. On cooling add water to the 250-cc. mark and filter the soln. Combine 50 cc. of the water soln. and 50 cc. of the soln. obtained with the citrate soln. and det. the phosphoric acid according to the molybdate in the citrate method. To ppt. the phosphoric acid by the citrate method add 25 cc. of a soln. contg. per l. 50 g. of $MgCl_2$, 70 g. of NH_4Cl, 61.6 g. of citric acid and 625 cc. of ammonia (d. 0.91). The ppt. should be allowed to stand for a considerable time, best overnight. J. DAVIDSON

Basic slag vs. acid phosphate. C. E. THORNE. Ohio Agr. Expt. Sta., *Mo. Bull.* **5**, 91–3, 141–6(1920).—A comparison of the two materials as a source of P in field plots is made. The data as figured on a money value show that basic slag is no more valuable than acid phosphate. J. J. SKINNER

The calcination of phosphates for the manufacture of fertilizers. E. SCHMIDT. *Kunstdünger, Futterm Leim* **17**, 269–70, 282(1920); *Chimie & industrie* **6**, 68(1921).—Outline of 9 different processes for the prepn. of fertilizers from phosphates. A. P.-C.

Raw phosphates as fertilizers. A. GEHRING *Centralblatt Kunstdüngerind.* **25**, 13–5(1920); *Chimie & industrie* **5**, 582(1921).—Account of tests carried out by Lemmermann on the use of raw phosphates as fertilizers, consisting essentially in making acids react with the phosphate after the latter has been applied to the soil. KNO_3 imparts an alk. reaction to soil, while $(NH_4)_2SO_4$ gives an acid reaction. When the soil is originally acid the plants can stand a certain amt. of additional acidity but it may have an unfavorable influence. Lemmermann utilizes the acidity developed by $(NH_4)_2SO_4$ by using it along with raw phosphate. Koch and Kröler have pointed out that the soil acids (especially CO_2) can also be used to render raw phosphates sol. If too much NH_3 is produced by bacterial action, it will neutralize the acid formed. Liquid manure treated with H_2SO_4 is admirably suited, for it contains $(NH_4)_2SO_4$ and supplies a favorable medium for the development of bacteria. A. P.-C.

The effect of potassium salts on the anatomy of Dactylis glomerata. O. N. PURVIS. *J. Agr. Sci.* **9**, 338–65(1919).—The material selected for this investigation was collected from the plots at Rothamsted which were treated for 60 yrs. with the following applications of fertilizers.

Plot.	Fertilizer.	$(NH_4)_2SO_4$.	Superphosph.	K_2SO_4.	Na_2SO_4.	$MgSO_4$.
		Lbs.	Cwts.	Lbs.	Lbs.	Lbs.
7	Complete minerals	...	3.5	500	100	100
8	Minerals, no K	...	3.5	..	250	100
9	Complete minerals + NH_3	400	3.5	500	100	100
10	Minerals, no K + NH_3.	400	3.5	...	250	100

Specimens of the third internode below the inflorescence were collected at intervals during the summer of 1917, on May 31st and June 8, 15, and 26. The thickness of the wall, the diam. of the lumina and ratio of the lumen to the wall were measured both in sclerenchyma and metaxylem elements which showed that in the early stages the sclerenchyma walls were thinner where K had been supplied, but this effect disappeared

later in the season. The lumina were larger in plants receiving K when nitrogenous fertilizers were used, but with NH_4 salts present this effect was reversed. In the xylem the thickness of the walls remained the same in the presence or absence of K salts. When no N was added through the fertilizers the diam. of the lumen was decreased in the presence of K, but when NH_4 salts were present, the diam. was increased by the application of K. K produced an increased ratio of lumen to wall but this effect gradually passed off. P. concludes from these results that the rigidity of plants supplied with K salts is not the result of anatomical strengthening, but must be attributed to some other cause, as the influence of the salts on the physiological condition, or the chemical compn. of the plant. R. B. DEEMER

The need for lime and how to meet it. B. H. BEDELL. *J. Ministry Agr.* **28**, 200–6(1921).—A general discussion. J. J. SKINNER

The value of magnesium sulfate as a fertilizer. A. JACOB. *Chem.-Ztg.* **45**, 445–7 (1921).—Preliminary expts. showed that the use of $MgSO_4$ as a fertilizer resulted in increased yields of potatoes. See *C. A.* **15**, 1055. J. DAVIDSON

Experiments to determine the value of bat guano as a fertilizer. WM. A. ALBRECHT. Missouri Agr. Expt. Sta., *Bull.* **172**, 39 pp.(1921).—For the production of NH_3 in soils bat guano is equal to dried blood and tankage. In producing nitrates it is not equal to dried blood but is superior to tankage. RUSSELL M. JONES

The fertilizer value of cotton bush. ANON. *Agr. J. India* **16**, Pt. II, 209(1921). —The amts. of N, P and K returned to the soil by burying the old plants are greatly in excess of those removed by seed and lint. Av. samples of the material contained 2.16% N, 1.40% P_2O_5 and 2.35% K. RUSSELL M. JONES

The breaking down of certain organic fertilizers. RIPPERT. *Kunstdünger Futterm., Leim.* **17**, 66(1920); *Chimie & industrie* **5**, 81–2(1921).—On treating horn meal with 20% of KOH in soln. most of it dissolved with the liberation of a small amount of NH_3. The soln. was filtered and evapd. on the water-bath, yielding a brownish, brittle mass, easily and completely sol. in cold water. Blood meal is not so completely broken down by this treatment. Pot expts. on oats gave the following amts. of grain and straw resp.: no fertilizer, 2.5 and 18.0 g.; 1 g. of N in the form of horn treated with 20% KOH, 11.5 and 75 g.; 1 g. of N in the form of gelatin treated with 20% KOH, 10 and 57 g.; 1 g. of N as $(NH_4)_2SO_4$, 10 and 55 g. Each pot was supplied with a sufficient amt. of K_2O and P_2O_5. Another series was carried out with blood meal and with bone meal treated as follows: the meal was mixed with a soln. of molasses undergoing vigorous lactic fermentation, allowed to stand for 4 wks., and a little more molasses added. When the biological decompn. was complete, the liquor was evapd. on the water-bath, and was used for pot expts. on mustard. The N content of the blood meal was: before treatment 5.432% total, 1.042% sol.; after treatment 3.374% total, 1.237% sol. The N content of the bone meal was: before treatment 3.321% total, 0.797% sol.; after treatment 2.805% total, 1.189% sol. Some of the N is lost during fermentation. The pot expts. gave the following yields of green material on adding to the base fertilizer: K_2O, P_2O_5, no N — 18.05 g.; 10 g. of untreated blood meal — 59.5 g.; 10 g. of treated blood meal — 88.5 g.; 10 g. of untreated bone meal — 27.5 g.; 10 g. of treated bone meal — 50.5 g. The fertilizers obtained by biological decompn. may be used dry. But it is preferable to absorb the liquid in dry peat, which has the double advantage of eliminating evapn. and keeping the bacteria alive. A. P.-C.

Effect of weathering and storage upon the composition of barnyard manure. M. F. MULLER AND F. L. DULEY. Missouri Agr. Expt. Sta., *Bull.* **172**, 40(1921).—After 5 months' exposure to the weather, manure stored in a pan without drainage, or in a conical pile on the ground, lost $^1/_3$ its dry matter, while that stored in a pan having drainage lost 45%. The loss of N in the conical pile was slightly less than that in the undrained pan

but the loss of potash was 5 times as great. The manure in the drained pan lost 47% of its K. RUSSELL M. JONES

Report of the chemist and assistant chemist. L. G. WILLIS AND J. D. CARRERO. Porto Rico. Agr. Expt. Sta., *Ann. Rept.* **1920**, 13–15.—By means of pot expts. with rice, it is shown that P has a tendency to cause a chlorotic condition of the plant due to faulty assimilation of iron. NH_4 salts, except phosphate, were preferable for neutral or basic soils and nitrates gave best results on acid soils. The use of $(NH_4)_2SO_4$ increased acidity in comparison to $NaNO_3$. H_3PO_4 added to a basic soil gave good increases in yield. J. J. SKINNER

The use of ferruginous sands in viticulture and arboriculture. ED. CROUZEL. *Repert. pharm.* **33**, 129–31(1921).—The use of ferruginous sands is recommended as a source of iron for vineyards and orchards. This recommendation is made on the basis of theoretical considerations and on the basis of results obtained in parks and orchards. J. DAVIDSON

Summary of the results of plot tests for cane culture in Java. XII. Tests with furnace ashes, molascinder, molascuit, molastego and molastella, up to the year 1918. J. KUYPER. *Arch. Suikerind.* **29**, 591–654(1921); cf. *Arch. Suikerind.* **25**, 1638; *C. A.* **14**, 3333.—The results of 185 field expts. with furnace ashes, made between 1909 and 1918, are given in great detail in a number of tables, and are fully discussed. They lead to the following conclusions: Furnace ashes rarely give noteworthy increases in yield of cane, except on certain soil types. The results are generally more pronounced on soils poor in P and on heavy soils, but sometimes light soils or soils rich in P respond quite well. The ashes act, therefore, mainly as a P fertilizer and mechanical ameliorant. They have no value in Java as K fertilizer. The effect of the ashes appears principally in the cane yields, but the sugar yield is also increased in most cases. One bucket per row is usually sufficient. The ashes are first sifted to remove lumps, applied, and worked in, ahead of other fertilizers. The best results from ashes may be expected on the older lands in certain districts, also on some heavy clays, and some moist sandy grounds. Molascinder, which is also advertized as a fertilizer, consists of a mixt. of 100 parts molasses, 250 parts ashes, 100 parts filter press cake, 60 parts stable manure, 30 parts bagasse meal. A number of expts. with this material have shown it to be of very little value. Molascuit and molastego are mixts. of molasses with bagasse meal, while molastella is made from molasses and cassava residues. If these have any fertilizing value at all, it is due solely to the molasses they contain. F. W. ZERBAN

Cotton tolerance to alkali in the field. C. N. CATLIN. Arizona Agr. Expt. Sta., *Ann. Rept.* **30**, 408–9(1919).—Good cotton is produced in soil low in chlorides and containing 0.4% of sol. salts. It is unprofitable to raise cotton on soil containing 0.4% to 0.6% of sol. salts where 0.1% to 0.3% is chlorides. The total destruction of the crop occurred on soils containing upward of 0.6% sol. salts, of which one-half or more was chlorides. A. A. RILEY

Resistance of crops to alkali. A. E. VINSON AND C. N. CATLIN. Arizona Agr. Expt. Sta., *Ann. Rept.* **29**, 342–5(1918).—A series of analyses is given illustrating the resistance of cotton and other crops to alkali under field conditions. A table shows the resistance of various crops to alkali under field conditions. A. A. RILEY

The relation of salt proportion to the growth of wheat in sand cultures. E. VAN ALSTINE. New Jersey Agr. Expt. Sta., *Ann. Rept.* **32**, 366–74(1919).—Wheat was grown in sand cultures with Shives 3-salt soln. The work was carried out on coöperation with the National Research Council, special committee on salt requirements of agr. plants. The triangular diagram is used in presenting the results; KH_2PO_4, $Ca(NO_3)_2$ and $MgSO_4$ are the salts used. The results are given in tables and diagrams. The highest yields of tops occur where low amts. of KH_2PO_4 and $Ca(NO_3)_2$ with higher

proportion of $MgSO_4$ are used. Higher transpiration is correlated with large growth of tops and roots and low transpiration with low yields. H-ion concn. was detd. in the cultures. The reaction of the solns. was changed by the plants towards neutrality. High yields in general are correlated with large differences in the p_H values and low yields with small differences. The manner in which plants bring about the change is not detd. A. A. RILEY

Fertilizer experiments on pecans conducted by the United States Department of Agriculture. J. J. SKINNER. *Proc. Ga.-Fla. Pecan Growers' Assoc.*, Cairo, Ga. 1921, 4-11.—Fertilizers high in N were most effective in increasing growth of young pecan trees. Production of nuts on older trees was most benefited by a fertilizer high in P. For max. growth and nut production a fertilizer contg. all 3 fertilizing constituents (P, N, and K) is required. J. J. SKINNER

The sewage irrigation field on the city of Dülmen. A. KREUTZ. *Landw. Jahrb.* **52**, 741-68(1919); *Expt. Sta. Rec.* **44**, 381.—A description of the field used for sewage disposal is given. The sewage is applied directly to the field by means of flooding. Analysis of the raw sewage and drainage water showed that the N and P_2O_5 content of the sewage was absorbed by the soil, but some K was not absorbed and was lost in the run off water. J. J. SKINNER

Some of the effects of the war upon fertilizers. L. L. VAN SLYKE. New York Agr. Expt. Sta., *Bull.* **471**, 10 pp.(1920).—The number of complete fertilizers in the state decreased from 614 in 1914 to 171 in 1919. Mixts. of P and K disappeared by 1916 and mixts. of P and N appeared in large numbers. The av. % of N decreased after 1915 and that of K decreased greatly after 1914. The cost of fertilizers increased greatly. J. J. SKINNER

The agricultural utilization of explosives containing ammonium nitrate. FELICE GARELLI. *Ann. accad. agr. Torino* **62**, 75-80(1919).—The explosive is systematically leached with H_2O until a concn. of 25-26° Bé is reached when the soln. is mixed with powdered peat (160 l. soln. to 100 kg. peat). The product contg. 40% H_2O dries easily when exposed to the air and stirred at intervals. The resultant product has the nitrate uniformly distributed, is amphoteric to litmus paper, keeps well, is dry and pulverulent and not dangerous to handle. ALBERT R. MERZ

The fight against plant parasites. A. KÖLLIKER. *Chem.-Ztg.* **45**, 460-1(1921).—A comprehensive review of the present status of insecticides and fungicides. J. DAVIDSON

Dipping and fumigation of nursing stock. K. C. SULLIVAN. Missouri Agr. Expt. Sta., *Bull.* **177**, 1-36(1921).—HCN did not in every case completely control the San Jose scale. Gas used at a strength of 1-1-3 gave better results than the weaker strength of $^1/_2$-$^1/_2$-$^1/_2$. All strengths of HCN used caused more or less injury to the plants. The 1-1-3 formula is recommended for nursery stock. CS_2 did not control the scale and caused a very high percentage of injury. Lime-sulfur used at 1-9 and 1-7 strengths gave fairly good results in controlling the scale. Miscible oil gave the best results. Tops only should be dipped. Lemon oil or nicotine sulfate should not be used as dips for controlling scale on nursery stock. RUSSELL M. JONES

Cyanide gas remedy for scale insects. C. P. LOUNSBURY. *J. Dept. Agr. Union S. Africa* **2**, 437-52(1921).—Outlines and gives details of a simple and effective method for fumigation. L. declares HCN gas fumigation is the cheapest and most effective method for the suppression of Red Scale and other "hard" scale insects in com. plantings of citrus trees. C. B. DURGIN

De Haen's colloidal solution of sulfur as a spray against plant pests. HUGO KUHL. *Chem. Ztg.* **45**, 479-81(1921).—A colloidal soln. of S has been prepd. as a spray against certain fungus plant diseases. It is especially effective against mildew. The S is sub-

microscopic and behaves as a perfect colloid when pure, but small amts. of impurity greatly affect its colloidal properties. The extreme fineness of division gives it a good covering power and renders it effective as a fungicide. Used on several kinds of plants in 0.05% soln., it causes no injury to the leaves. The material discussed is prepd. by the de Haen Company of Hanover, Germany. M. S. ANDERSON

Studies on the *Azotobacter* (KAYSER) **11C.** Determination of phosphoric acid as magnesium pyrophosphate (BALAREFF) **7.** Composition of our crops in successive periods of growth (MASCHHAUPT) **11D.** The influence of the nature of the soil and fertilization on the content of nitrogen and ash constituents in crops (MASCHHAUPT) **11D.** Azotobacter chroöcoccum (BONAZZI) **11C.** Utilization of spent oxide from gas works (WAGUET) **21.** The conditions effecting the quality of the Java indigo plant (DAVIS) **25.** Electrical treatment of hot slags to prepare fertilizers, etc. (U. S. pat. 1,377,554) **9.**

Basic Slags, their Production and Utilization in Agriculture. London: Faraday Society, 10 Essex St. Strand. W. C. 2. 7s 6d. For review see *Intern. Sugar J.* **23,** 407(1921).

KRISCHE, P.: **Agrikulturchemie.** Berlin und Leipzig: B. G. TEUBNER. For review see *Z. angew. Chem.* **34,** Aufsatzteil 171(1921).

Fertilizer. P. SCHMIDT. U. S. 1,378,284, May 17. A fertilizer containing $Mg(OH)_2$ and lime is prepd. by treating lime with a soln. of $MgCl_2$ or $MgSO_4$.

Ammonium aluminium sulfate. E. L. PEASE. Brit. 162,314. NH_3 is extd. from gases such as producer gas by passing them over a dry product contg. $Al_2(SO_4)_3$ obtained by burning shale or other aluminous material such as clay together with S or a material which on burning yields SO_2; or a S-bearing shale may be burnt alone. The product obtained by the absorption of NH_3 is suitable for use as a fertilizer.

16—THE FERMENTATION INDUSTRIES

H. S. PAINE

An electrochemical method for the determination of the acid energy of wines. LUIGI CASALE. *Staz. sper. agrar. ital.* **53,** 298–308(1920).—The method of calcn. proposed by C. (*C. A.* **15,** 919) requires a knowledge of many analytical data before it can be used. The present method makes use of the principle of isohydric solns. The app. consists of (*a*) a Mariotte bottle with a stopcock, (*b*) a glass U tube of 10–12 mm. diam. and (*c*) 2 cylindrical glass vessels of approx. 600-cc. capacity with Cu electrodes. The Mariotte bottle above contains H_2O which can flow into the lower part of the vessel contg. HCl or other acid. This is provided with 2 side openings, one for entrance of the H_2O, the other for exit of the excess liquid. The liquid to be tested (wine) is placed in the other vessel which is closed with a three-hole stopper through which are passed the U tube, the Cu wire attached to the electrode and a capillary serving as a condensation tube for alc. volatilized. The 2 Cu electrodes should be of equal surface and well cleaned. Communication is established between the 2 vessels by means of the U tube which is filled with either of the liquids. After immersion of the electrodes the Cu wires leading from them are joined to a galvanometer. H_2O is permitted to descend at intervals into the first vessel and its contents are agitated. As the diln. increases the deviation shown by the galvanometer approaches zero. When a const. zero reading is reached 25 cc. of the dil. acid is titrated with 0.02 *N* alkali. The vol. *V* contg. 1 g. mol. of the

acid is calcd. and the dissociation (m) is detd. by the equation $m=\frac{VK-+\sqrt{V^2K^2+4VK}}{2}$ where K is the dissociation const. Then m/V is the H-ion concn. of the wine or other liquid examd. The whole app. is placed in a thermostat at 70° during the detn. Results obtained indicate a lower acid energy (H-ion concn.) of wine than that calcd. which is also the case with results obtained in the inversion of sucrose, which gives even lower results. Lack of agreement is due to the action of alc., which diminished the dissociation, being disregarded in the method of calcn. and because in the electrochemical and inversion methods the temps. of the acid solns. are 70° which results in less dissociation. ALBERT R. MERZ.

Application of the electrochemical method for the determination of the acid energy of wines. LUIGI CASALE. *Staz. sper. agrar. ital.* **53**, 395–8(1920).—The app. (see preceding abstr.) may be considered a cell in which the p. d. at the poles (V_0) is equal to the e. m. f. (e) minus the fall of potential due to internal resistance (r_0), or $V_0=e-r_0i$, where i is the intensity of the current. By Ohm's law, $i=e/(r_0+R)$, where R is the external resistance. Whence $V_0=Ri$. Consequently the dilu. of the acid is stopped before it becomes isohydric with the wine. If it be considered that the zero reading of the galvanometer is reached when $e=r_0i$, the operator can reduce r_0i (in which i is already very low) to an insignificant value by diminishing r_0 and he will thus have at the zero reading an e and a V_0 of insignificant value. r_0 may be diminished by increasing the surface of the Cu electrodes and by diminishing the distance between them. The value of r_0i, however, is never zero and however small it is the zero reading of the galvanometer is reached before the acid has undergone the dilu. desired. Increase of temp. increases the velocity of the ions of the completely dissociated HCl while it decreases the dissociation of the dissolved electrolytes of the wine. If the action of the temp. in diminishing the acid energy (H ion concn.) of the wine and consequently in increasing the dilu. which the acid must undergo is equal to the action which the product r_0i has in lowering the dilu. which the acid must undergo there is exact compensation. A. R. M.

A new method for the determination of glycerol in wine by transformation into acrolein with the aid of boric acid. A. HEIDUSCHKA AND F. ENGLERT. *Z. anal. Chem.* **60**, 161–6(1921).—By heating glycerol with boric acid, acrolein is formed which by absorption in concd. NH_4OH can be easily changed to aldehyde ammonia. This last compd. reacts with $AgNO_3$ to form metallic Ag and the excess of $AgNO_3$ used in an analysis may be detd. by titration. The procedure is as follows: Place the extract from 100 cc. of wine and about 15 cc. of water in a 50-cc. quartz retort and evap. carefully with the retort open, heating in a bath of molten metal (8 pts. Pb, 3 pts. Sn and 8 pts. Bi). As soon as the liquid is reduced to about 2 cc. add 1 g. of H_3BO_3 and heat until no more steam is evolved. Then allow the retort to cool somewhat and place in front of it two Péligot tubes each contg. 20 cc. of 25% NH_3 soln. kept cold by immersing the tubes in ice. Insert in the tubes of the retort a glass tube drawn out fine which is connected with a gasometer contg. air. When the app. is all connected up, heat carefully until the temp. of the bath reaches 320°. The contents of the retort froth and at 250° begin to decomp. and acrolein is formed from the glycerol. Introduce a slow stream of air from the gasometer and heat at 320° for 45 min. Rinse out the contents of the absorption tubes into a beaker contg. 5 cc. of 0.1 N $AgNO_3$ soln. and heat the contents of the beaker until there is only a faint odor of NH_3 in the vapor. The reduction of the $AgNO_3$ soln. takes place after 15 or 20 min. when most of the excess NH_3 has evapd. Filter through a glass-wool filter and to the filtrate add HNO_3 and ferric alum indicator and titrate the excess Ag^+ with 0.1 N NH_4CNS soln. The conversion of the glycerol into acrolein is by no means complete and the glycerol content must be estimated by a table which is prepared by subjecting varying wts. of glycerol to analysis

by the above method and detg. how many cc. of standard $AgNO_3$ soln. are reduced in the expt. Thus 0.230 g. of glycerol corresponded to 0.31 cc. of $AgNO_3$ soln., 0.50 g. glycerol to 0.61 cc., 1.01 g. glycerol to 1.28 cc. and 1.50 g. glycerol to 1.49 cc. In testing the method 6 wines were analyzed as above, by the lime method of Neubauer and Borgmann and by the iodide method of Zeisel and Fanto. The values obtained ran a little lower with the acrolein method than with the other methods but there is reason to believe that the lower results are nearer the truth. W. T. HALL

Ebulliometric determination of alcohol in wines. UGO PRATOLONGO. *Giorn. chim. ind. applicata* **3,** 143–7(1921).—In a critical and exptl. investigation of the method and the factors contributing to errors in the use of the ebulliometric method of alc. detn. P. drew the following conclusions: (1) From the point of view of ebulliometric behavior in H_2O-alc. solns., the constituents of wine fall into 2 groups: (*A*) comprizing glycerol, tartaric acid and presumably the tartrates, malates, succinates, citrates and the other fixed salts of wine—these have a normal or nearly normal ebulliometric behavior; (*B*) comprizing glucose, fructose, AcOH and lactic acid and their salts—these have an abnormal ebulliometric behavior. In respect to AcOH and lactic acid, the abnormality of behavior is sufficiently accounted for by their volatility. In respect to glucose and fructose the reason for the abnormality is less clear; it is probably due to a constitutive influence. (2) With H_2O-alc. solns. of low content (up to 3% alc.) the ebulliometric behavior of the constituents of wine is practically normal. The addition of each simple constituent of wine raises the b. p. of the H_2O-alc. solvent mixt. proportionately, *i. e.*, about 0.51° for the addition of a gram mol. of solute to 1 l. of solvent. The increase of boiling point varies with the dilu. of the H_2O-alc. mixt. caused by the addition of solute, but only partially. If the ebulliometric reading is assumed according to the alcoholic titer of the mixt., the results will have a minus error. (3) With wines of high alcoholic titer (12–18%) only one group of the constituents of wine, *i. e.*, tartaric acid and presumably malic, succinic and citric acids and their salts, maintain their normal ebullioscopic behavior; while the other group, *i. e.*, glucose, fructose, AcOH, lactic acid and their salts present abnormal ebullioscopic behavior. Glucose and fructose give the more anomalous effects as the alcoholic titer increases. (4) With wines of intermediate alcoholic titer (3–12%) the 2 opposing influences exactly compensate each other. (5) An ebulliometer graduated on a basis of H_2O-alc. solns. and used in the detn. of alcoholic content in ternary and quaternary and even more complex mixts., such as wine, will, in general, give results which are too low, for mixts. of alc. content up to 3%, almost exact, for mixts. from 3–12%, and too high, for mixts. of alcoholic content from 12–18%, especially if sugar is among the dissolved compds. A trigonal diagram is given showing the b. p.'s of an alc.-H_2O sugar soln. ROBERT S. POSMONTIER

The causes determining the disappearance of coal-tar dyes in wine. A. MAZZARON. *Staz. sper. agrar. ital.* **53,** 172–83(1920).—Expts. show that light is the principal if not exclusive agent in the phenomenon, though its action is dependent on the presence of substances naturally contained in or added to the wine (lactic, malic and citric acids, SO_2, sulfites, etc.). The action may be either one of reduction or oxidation. Enotannic and other substances naturally contained in wine do not appear to form precipitable compds. with the artificial dyes, since enocyanine and enotannic acid when added to artificially colored water do not give ppts. and since the color disappears from some sterilized and artificially colored wines without pptn. Microörganisms which change the normal compn. of the wine do not appear the direct and sole cause of the disappearance though they may indirectly aid by producing substances which facilitate the destructive action of the light on the artificial dye. ALBERT R. MERZ

The question of the plastering of wine. GAETANO MAGNANI. *Staz. sper. agrar. ital.* **52,** 584–6(1919).—Polemical. Cf. Borntraeger (*C. A.* **15,** 919). A. R. M.

The question of the plastering of wine. ARTURO BORNTRAEGER. *Staz. sper. agrar. ital.* **53**, 184–6(1920).—A reply to Magnani (cf. preceding abstract). A. R. M.

The cinchona-treated wine industry in Piedmont. G. PIANO. *Staz. sper. agrar. ital.* **52**, 290–304(1919).—Sugar and alc. are added to the wine which is then made bitter by means of Peruvian bark. This is done either by steeping finely powdered calisaya bark in the wine for 5 days at about 50°, with frequent shaking in closed vessels to avoid the loss of alc., or by adding an alc. ext. of the cinchona to the fortified wine. Chem. analyses are given of 56 such wines and the alkaloid content of 15 of them was detd. Their alc. content varies from 10.35 to 20.25% by vol.; the sugar content, from 3.49 to 20.7%. The ext., deducting sugar, varies from 1.4 to 6.0%; acidity from 0.217 to 0.765%; and volatile acidity from 0.036 to 0.255%. Ash runs from 0.124 to 0.386%; glycerol, 0.337 to 0.829%; alkaloids, 0.034 to 0.097%; and alkalinity of the ash, 4 to 25. In chem. compn. they show a marked similarity to vermouth. A. R. M.

The manufacture of tartaric acid in the Argentine Republic. M. L. PONDAL. *Anales soc. quim. Argentina* **7**, 304–16(1919).—Tartaric acid is produced in large quantities from the refuse from wine making. The refuse, consisting of stems, skins, seeds, and settlings from the wine vats, is finely ground and boiled with water for 2–4 hrs. under a pressure of 4 atm. The mixt. is then run into tanks, acidified with H_2SO_4 and filtered. The filtrate is treated with milk of lime and the ppt. of Ca tartrate which forms is filtered off and drained in a centrifugal. The Ca tartrate is treated with a slight excess of dil. H_2SO_4, $CaSO_4$ is filtered off, and the acid soln. is treated with animal charcoal and enough $K_4Fe(CN)_6$ to ppt. the iron present, filtered again, evapd. in lead-lined vacuum pans, and crystd. in lead tanks. L. E. GILSON

Molecular concentration of the juices of grape vines. A. CAUDA AND C. MENSIO. *Staz. sper. agrar. ital.* **53**, 317–31(1920).—The liquid flowing naturally from cuts of the vine branches (pianto di vite) is rich in mineral and org. substances. The harmonic av. of its elec. cond. is 69.3×10^{-5} (arithmetical av., 81.5×10^{-5}) with extremes of 34×10^{-5} and 129×10^{-5} for the 89 samples examd. The juice expressed from the vine branches and from the bunches of green grapes has a very much higher elec. cond. Early maturity and inherent vigor are indicated by high elec. cond. of the "pianto di vite." The elec. cond. is influenced by the org. substances, especially those of acid reaction, as well as by the mineral substances in soln. There is no strict relationship between the ash and the solid ext. though the ash ordinarily constitutes $^1/_4$ to $^1/_2$ of the total solid ext. The elec. cond. increases with content of ash and with a const. quantity of ash it increases with the % of ext. There is a direct ratio of proportionality between the acidity and the % of solid ext. of "pianto di vite" and the elec. cond. increases with the degree of acidity. The cond. increases with the season of growth reaching a max. and then decreasing for the same vine. Variations exist in the concn. of the "pianto di vite" between vines of the same place, between those grafted and those not grafted, and according to the system of cultivation, vigor and age. Vines grafted on American stocks give more concd. "pianto di vite" than the same varieties non-grafted. High elec. cond. probably corresponds with high yields of grapes. ALBERT R. MERZ

The white cherry industry. G. PARIS. *Staz. sper. agrar. ital.* **53**, 187–231(1920).—The successive steps of the industry are described in detail. The treatment with SO_2 for preservation is carried on empirically and suggestions are made for obtaining better results. P. concludes from results of expts. that "org. substances of a colloidal nature such as cellulose, pectic and albuminoid substances can absorb SO_2 but very labile products are formed which are easily dissociated by the simple action of H_2O. They are evidently not true compds. Relations of a chem. nature can exist between glucose and SO_2 but the compd. formed is so easily dissociated that according to phys. tests it does not appear that the said compd. forms." Malic and tartaric acids do not fix SO_2. ALBERT R. MERZ

Wine made from dried figs. E. GARINO-CANINA. *Giornale vinicolo italiano* **45**, No. 30, 260–1; *Bull. Agr. Intelligence* **10**, 990–2.—Dried figs were extd. with 3 parts of H_2O, the must was filtered, and fermentation induced by saccharomycetes at 28°. The fermented liquor was golden yellow, with a taste at first like beer, becoming bitter in time. The total acidity of the wine was low, with almost no tartaric and little succinic acid relative to the EtOH. The EtOH content was 6.34% by wt. and the d_{15} 0.9939. N compds. 0.035%, pentosans 0.08% and the ash 0.32% (SO_3 0.0695 and P_2O_5 0.052) were all essentially higher than in grape wine. C. C. DAVIS

Chemico-biological study of microörganisms injurious to wine making. E. GARINO-CANINA. *Rivisti di Ampelografia* **1**, No. 1, 2–6; *Bull. Agr. Intelligence* **11**, 387–9.—Cultures of *Saccharomyces ellipsoideus* (A), *Willia anomala* (B), *Pichia membranaefaciens* (C), *Dematium pullulans* (D), *Penicillium glaucum* (E), and *Botrytis cinerea* (F) were sown in the must of the "favorita" grape, previously sterilized. After 50 days at 24° they were analyzed. **B, C,** and **F** did not diminish the total acidity because of increase in volatile acids and lactic acid, though considerable malic acid was attacked. Dextrose and levulose were consumed to the same extent. **D** and **E** diminished the total acidity without producing an equiv. amt. of volatile acids. Both sugars were attacked. **E** destroyed acids most actively, consuming 0.9 of the malic acid. With addition of 0.179 g. of SO_2 per l., **A** caused regular fermentation after 48 hrs. inhibition. The others did not develop in the same SO_2 medium and fermentation ceased in 25 days. C. C. DAVIS

New method for the preparation of glycerol. ANON. *Wärme u. Kalte-Techn.*, Jan. 1920; *Chimie & industrie* **5**, 326(1921).—A so-called biochem. method consists in fermenting a 10% sugar soln. to which have been previously added a little K_2CO_3, MgO, and phosphoric acid, then 10% of yeast (on the wt. of sugar), and finally some Na_2SO_4 or other salt which will give an alk. constitution to the fermenting liquor. The glycerol is sepd. from the alc. by distn. The yield is 40%, while usual processes give about 3%. A. P.-C.

The fruits of Melia azedarach—their possible use for manufacture of alcohol. L. RIGOTARD. *Bull. mensuel du jardin colonial* [new series] **3**, 186–8(1919); *Bull. Agr. Intelligence* **10**, 993–4.—The fruits of *Melia azedarach* (Indian or Chinese lilac), found in Morocco when mature, is of the size of a cherry, nearly spherical with fleshy pericarp, soft and whitish in color, with nauseating odor. The stone contains 3 or 4 kernels. Air-dried, 100 fruits weigh 81.1 g., 100 stones 30.0 g. and 100 kernels 5.0 g. The pulp showed H_2O 9.44, ash 4.48, nitrogenous matter (1.9 × 6.25) 12.15, direct reducing matter as glucose 27.0, sucrose after inversion 2.88, total sugar 29.88%. As the fruit appears to be fairly poisonous its sugar content suggests its use for the manuf. of alc. by fermentation and distn. The kernels are oily. H. A. LEPPER

Industrial (including power) alcohol. CHAS. H. BEDFORD. *J. Roy. Soc. Arts* **69**, 471–86(1921).—A general discussion of the possible sources of alc. within the British Empire and the best methods of denaturizing the alc. for industrial use. It is stated that a plant is being erected at Rangoon (India) for the manuf. on a com. scale of *alc. from rice straw.* The process is not described. L. E. GILSON

Raw materials for industrial alcohol production (in South Africa). CHAS. F. JURITZ. *S. African J. Ind.* **4**, 167–75(1921).—Sugar beets are a possibility but are not cultivated in S. Africa at present. Potatoes and maize give low yields per acre compared with other countries. A small amt. of cane molasses is available. Sweet potatoes are suggested as the most hopeful possibility. L. E. GILSON

Investigation into the settling caused by a sudden cooling of fermenting yeast or yeast which has already fermented. H. MILL. *Z. ges. Brauw.* **43**, 49–51, 57–8(1920); *Chimie & Industrie* **5**, 456(1921).—In a brewery using pure yeast fermenting normally

at 6–8° the temp. of the cellar dropped to 0° and remained there for 34–6 hrs. The yeast settled out with difficulty, the wort remaining milky, and this characteristic persisted for several generations. M. carried out an investigation by cooling cultures in wort to 0° and between 15° and 19°, but observed nothing abnormal. It is nevertheless certain that cold affects the yeast as numerous dead cells are found after the cultures have been cooled during fermentation. A. P.-C.

The diseases of beers: their causes and remedies. R. HEUSS. *Z. ges. Brauw.* **43,** 121–3, 129–30(1920); *Chimie & industrie* **5,** 457(1921).—In several unstable beers, characterized by a sharp, disagreeable, and even putrid smell, the development of wild yeasts was disclosed. The presence of torula was often noted along with wild yeast. Methods of avoiding this trouble are outlined. A. P.-C.

Investigation into the possibility of using Delbrück's bacillus for the preparation of clear and stable beers. H. LÜERS. *Z. ges. Brauw.* **43,** 51–3, 58–61(1920); *Chimie & industrie* **5,** 456(1921). A. P.-C.

Chemical problems in the brewery. H. LÜERS. *Z. ges. Brauw.* **43,** 33–5, 41–2 (1920); *Chimie & industrie* **5,** 456(1921). A. P.-C.

Chemical-physiological studies of the yeast cell (SCHWEIZER) **11C.** Salt effect in alcoholic fermentation (HARDEN, HENLEY) **11C.**

EULER, H. and LINDNER. **Chemie der Hefe und der alkoholischen Gärung.** Leipzig: Akademische Verlagsgesellschaft. M. b. H. Gustav Fock. 350 pp. For review see *Nature* **107,** 485(1921).

Yeast. R. S. BENSLEY. Brit. 162,978, July 24, 1920. Yeast is prepd. by fermenting a mash prepd. by boiling potatoes in H_2O in which hops contained in a muslin bag are suspended, mashing the potatoes, and adding flour, sugar, salt, ginger, and the H_2O in which the potatoes were boiled. After fermentation, the mash is mixed with maize meal and the mixt. is spread out for some days until a dry product is obtained. The fermentation is effected either by brewer's yeast or by the dry product from previous operations.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Chemical composition of nim or margosa oil. K. K. CHATTERJI AND R. N. SEN. *Indian J. Med. Research* **8,** 356–62(1920).—This oil consists of stearic acid 28, oleic acid 36, margosic acid, $C_{30}H_{46}O_2$, 24%. H. V. ATKINSON

The origin of opium smoking. M. T. KOKS. *Pharm. Weekblad* **58,** 1037–51 (1921).—Oriental mystic lore concerning opium and the analogy to the philosophers' stone of the alchemists. A. W. Dox

Soaps medicated with corrosive sublimate. G. ISSOGLIO. *Giorn. farm. chim.* **70,** 5–8(1921).—Soaps containing $HgCl_2$ are no more antiseptic than ordinary soap. The Hg is present as an insoluble fatty acid soap. A. W. Dox

Computations in pharmaceutical technic. GIOVANNI ISSOGLIO. *Giorn. farm. chim.* **69,** 5–8, 29–35(1920).—A discussion of pharmaceutical arithmetic, and formulas to assist the pharmacist in computing dilns. A. W. Dox

Incompatibility of strychnine salts with glycerophosphates, cacodylates and sodium methylarsonate. A. DEMO. *Giorn. farm. chim.* **69,** 113–8(1920).—Pptn. of the alkaloid may be obviated by rendering the alkaloidal salt soln. neutral to phenolphthalein before adding the glycerophosphate, etc. A. W. Dox

Solubility of drugs in glycerol. K. HOLM. *Pharm. Weekblad* **58**, 1033–7(1921).—On account of the extensive use of glycerol as a solvent in pharmaceutical prepns. and the conflicting soly. detns. reported in the literature, the following solubilities were accurately detd. at 20°:

	Grams per 100 g. glycerol. Glycerol sp. gr. 1.23(86.5%).	Sp. gr. 1.26 (98.5%).
Lead acetate	129.3	143.0
Benzoic acid	1.18	2.0
Boric acid	13.79	24.80
Salicylic acid	0.985	1.63
Sodium biborate	89.36	111.15
Potassium bromide	20.59	17.15
Quinine sulfate	0.72	1.32
Potassium chlorate	1.32	1.03
Potassium iodide	58.27	50.70

A. W. Dox

Essential oil from the leaves of Skimmia laureola. J. L. SIMONSEN. *J. Soc. Chem. Ind.* **40**, 126–7T(1921).—The oil obtained by steam distn. from the leaves consisted mainly of *l*-linalyl acetate, while *l*-linaloöl, an unidentified hydrocarbon, and a complex mixt. of sesquiterpene alcohols and esters were likewise present. W. O. E.

Volatile oil from the leaves of Ocimum gratissimum, Linn. O. D. ROBERTS. *J. Soc. Chem. Ind.* **40**, 164–5T(1921).—The oil has the approx. compn.: terpenes (chiefly or entirely ocimene) 16.0%, phenols (eugenol) 55.0%, phenol ethers calcd. as Me chavicol 5.6%, alcohols (linaloöl) 13.0%, esters calcd. as $C_{10}H_{17}OH$ 0.6%, residue and loss 9.8%. In conclusion, reference is made to the volatile oil derived from the leaves of a large-leaf variety of *O. basilicum*, Linn., known in Java as "Selasih Mekah", which appears to be rather similar in compn. to the present sample. W. O. E.

A new water-soluble cresol preparation, "Fawestol." FRITZ DITTHORN. Berlin. *Centr. Bakt. Parasitenk, Abt. I* **80**, 374–9(1918).—Fawestol is a patented cresol prepn. having the same cresol content as crude cresol. It forms a clear aq. soln. up to 2.25%, which keeps indefinitely. In a 1% soln. it kills bacteria in 1 min. In a 2% soln. it is a complete substitute for a 5% cresol soap soln. Its solns. are neutral. J. H. L.

The use of lanolin in the manufacture of cosmetics. ANON. *Deut. Parfümerie Ztg.* **6**, 39–40(1920); *Chimie & industrie* **5**, 565(1921).—Review of the origin, prepn., compn., properties, and method of analysis of lanolin, from the point of view of its utilization in perfumery. A. P.-C.

Wax for sealing perfume bottles. W. DARSE. *Deut. Parfümerie Ztg.* **6**, 99–101, 112–3(1920); *Chimie & industrie* **5**, 445(1921).—Discussion of compns. with nitrocellulose bases and cellulose acetate bases used for hermetically sealing bottles of perfume. A. P.-C.

The adulteration of perfumes by means of phthalic esters. ANON. *Deut. Parfümerie Ztg.* **6**, 49–51(1920); *Chimie & industrie* **5**, 565(1921).—Phthalic esters, and more particularly neutral Me phthalate are extensively used as adulterants of essential oils. The adulteration is detected by saponifying and pptg. the acid out of the alk. soln. It can then be identified either as free acid or as anhydride. The author reviews the adulteration of essential oils of anise, bergamot, cassia, violet, lavender, mint, cinnamon, etc. A. P.-C.

Determination of alcohol in essences. W. OLSZEWSKI. *Pharm. Zentralhalle* **62**, 288–91(1921).—To 25 g. of the essence 25 g. of a satd. soln. of NaCl are added and the mixt. is extd. with 20 g. petr. ether, and the ext. washed with NaCl soln. The combined NaCl solns. are distd. and the amt. of alc. is detd. from the sp. gr. of the distillate.

H. A. SHONLE

Capsella bursa pastoris (shepherd's purse). CLEMENS GRIMME. Inst. f. angew. Bot. Hamburg. *Pharm. Zentralhalle* **62**, 217–220(1921); cf. *C. A.* **14**, 1002.—A review of the literature of 1920. H. A. SHONLE

Evaluation of lecithin. I. L. B. VAN DER MARCK. *Pharm. Weekblad* **58**, 989–92 (1921).—Lecithin is usually evaluated according to the procedure of Hager (Pharmazeutisches Praxis, Supplement). He uses an erroneous factor for calcg. the P content; and his procedure for detg. P (phosphomolybdate method) is tedious and liable to error. It is much simpler and quicker to det. P by neutralizing the excess H_2SO_4—HNO_3 with Na_2CO_3, adding NH_4Cl and then NH_4OH until a ppt. appears, dissolving in dil. HCl and pptg. as $MgNH_4PO_4$. The trace of Ca in lecithin is a slight but not serious source of error in this method. JULIAN F. SMITH

Aromatic plants of Indo-China. ANON. *Olien en Vetten* **5**, 503–4(1921).—A review. NATHAN VAN PATTEN

Some observations on eucatropine. L. E. WARREN. *Repts. Chem. Lab. Am. Med. Assoc.* **13**, 62–7(1920).—Eucatropine is a name adopted by the Council on Pharmacy and Chemistry for the substance known in Germany an euphthalmine. During the World War the supplies of this mydriatic became unavailable and the substance was made in this country. Eucatropine is closely related to β-eucaine. Theoretically it is β-eucaine in which a benzoyl group has been replaced by a mandeloxy group and in which H has been replaced by Me. In England the substance is called betacaine mandelate. The Am.-made product is a white, granular, odorless powder; permanent in the air; sol. in H_2O, EtOH, $CHCl_3$; insol. in Et_2O. The H_2O soln. gives ppts. with Na_2CO_3, I+KI, $KHgI_3$, $AuCl_3$, $KCdI_3$, picric acid and several other alkaloidal reagents. Ppts. were not given by $HgCl_2$, KI, $PtCl_4$, $PdCl_4$, $NaHCO_3$, $NaC_7H_5O_2$, or Na nitroprusside. The Au salt melts under H_2O at 100°, thus resembling atropine, the Au salt of which m. 100° under H_2O, but differing from homatropine and methylatropine. It does not give the Vitali test. It gave no ash on ignition. It lost 0.38% of its wt. on drying at 100°. On shaking out with $CHCl_3$ in presence of NH_4OH 86.09% of base was obtained. The substance contained Cl equal to 11.1% of HCl. The base was recrystd. from petr. ether; m. 111–2°. The Au salt m. 162° and contained 31.28% of Au. For comparison the reactions of atropine, hyoscyamine, scopolamine, methylatropine and eucatropine are tabulated. L. E. WARREN

Notes on the Bliss method for the separation of strychnine from quinine. L. E. WARREN AND A. H. CLARK. *J. Am. Pharm. Assoc.* **10**, 267–70(1920).—Sepn. of the alkaloids was attempted by the Bliss method (*C. A.* **14**, 450). The sepn. was not satisfactory; considerable strychnine was found in the fraction supposed to be quinine and a little quinine in the strychnine fraction. Known mixts. of the alkaloids in varying proportions were prepd. and were assayed by the Bliss method. The results showed that in all cases the method was unreliable. The quinine fractions invariably contained strychnine. In most cases the strychnine fraction was comparatively free from quinine so that the method may have a qual. value in detecting the presence of strychnine in mixts. The results for quinine were 110.5, 107.3, 106.8, 104.5, 101.0, 116.1, 104.7, 115.7, 102.2 and 101.3% of theory. For strychnine the findings were 11.7, 24.9, 27.8, 27.5, 80.5, 23.2, 28.5, 34.1 and 62.6% of theory. L. E. WARREN

Removal of the fluorescence of vaseline oils (MEYERHEIM) **22.** Evidence for the presence in digitalis of a principle that is eliminated rapidly after intravenous injection into the cat (DOOLEY) **11H.**

MARTIN, GEOFFREY. **Perfumes, Essential Oils, and Fruit Essences.** London: Crosby Lockwood & Son. 138 pp. 12s 6d net. For review see *Chem. Age* (*London*) **5**, 34(1921).

SCHWARZ, A.: **Hager's Pharmazeutisch-technisches Manuale.** Leipzig: Verlag von Joh. Ambrosius Barth. M 250, bound M 280.

TAPPEINER, H.: **Lehrbuch der Arzneimittellehre und Arzneiverordnungslehre.** Leipzig: Verlag von F. C. W. Vogel. 508 pp. Bound M + tax For review see *Chem. Ztg.* **45**, 440(1921).

Arsenical compounds. K. B. EDWARDS. Brit. 162,747, Jan. 29, 1920. Salts of thioarsenic acids, possessing the general formula $RAsO_{3-x}S_x$ and $R_3AsO_{4-x}S_x$ (in which R represents an alkali metal, NH_4, or an organic NH_4 radical), are prepd. by passing H_2S into a soln. of an arsenate, or by treating As_2O_3 or As_2S_3 with an alkali or $(NH_4)_2S_x$, or by treating As_2S_5 with an alkali or $(NH_4)_2S$, followed by double decompn. in the case of the organic compds. Examples are given of the prepn. of $Na_3AsO_3S.12H_2O$, $Na_3AsO_2S_2.10H_2O$, $Na_3AsS_4.8H_2O$, $NaAsS_2$, and of the analogous salts of $MeNH_2$ and $EtNH_2$. The substances are of use for the destruction of parasites externally.

Benzyl ester of 2-phenylquinoline-4-carboxylic acid. A. GAMS and O. KAISER. U. S. 1,378,343, May 17. Benzyl 2-phenylquinoline-4-carboxylate is prepd. as follows: Na 2-phenylquinoline-4-carboxylate is heated in acetone and treated with benzyl chloride, gradually added, the acetone is distd. off, the residue is mixed with water and extd. with ether or C_6H_6. The soln. in the volatile solvent thus obtained is washed with Na_2CO_3 and with H_2O and dried with $CaCl_2$ and then treated with dry gaseous HCl. The hydrochloride of the benzyl ester thus formed is a fine cryst. yellow powder. It is dissolved in alc., decompd. by adding solid Na_2CO_3 and sepd. by filtration from the NaCl. By concg. the soln. the ester crystallizes. It may be purified by recrystn. from alc. or ether. It m. 77–78°, is of a citron-yellow color, insol. in H_2O, readily sol. in C_6H_6 and oils and moderately sol. in ether. It is tasteless and is suitable for use as a therapeutic as a solvent of uric acid.

Depilatories. J. DONNER. Brit. 163,022, Oct. 5, 1920. A depilatory is prepd. in the form of a cream of ointment-like consistency or of a vanishing cream. The depilating agent may consist of the sulfides, polysulfides, or hydrosulfides of the alkali metals, earth metals or alk. earth metals, which may be suspended in a semi-solid soap emulsion or other vehicle. The emulsion may consist of soft soap and H_2O emulsified by means of a small quantity of caprylic alc. or a mixt. of 60 vol. diphenyl oxide and 40 vol. of amyl alc. An inodorous depilating agent may be formed by slaking quicklime with a 1% NaOH soln., adding sufficient 1% NaOH soln. to reduce this to a cream, passing H_2S through the mixt. until its action is neutral or only slightly alk., and then subjecting it to a low vacuum at 20–35° for removing excess H_2S. A cream may be formed of 100 g. of soft soap, 33 cc. of caprylic alc., and 120 cc. of H_2O to which is added 50 cc. of the above depilating agent. In place of soft soap any of the alkali salts of the fatty acids may be employed either alone or in combination with fatty acids, free alkali, glycerol, waxes, fats, resin, and oils. Bases which may be combined with a depilating agent comprize one or a mixt. of gelatinous or mucilaginous emulsoid colloids, such as agar-agar, tragacanth, gum arabic, gelatin, linseed mucilage, quince-seed mucilage, starch, pectin, flour, etc. Through mixt. with soaps, fats, waxes, paraffins, resins, etc., or gelatinous suspension of metals, metallic oxides, metallic hydroxides, or metallic salts, the product can be made to vary in transparency from slight opalescence to opacity. The depilatory may be perfumed or colored or both.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Study of the distillation of nitric acid and of mixtures of sulfuric and nitric acids. PAUL PASCAL (AND M. GARNIER). *Ann. chim.* **15**, 253–90(1921).—A rept. of the most com-

plete study yet made of the vapor pressures and partial pressures of HNO_3 and mixed acid solns. at various pressures. For HNO_3, results were obtained which checked those of Creighton and Githens (*C. A.* **9**, 744) fairly well, though in both cases exptl. difficulties were encountered at the higher temps. and pressures, owing to decompn. of HNO_3, which gave a low b. p. The difference between the apparent b. p. and the true b. p. was greatest at about 500 mm.; at higher pressures the effect of the pressure was greater than that of the increased temp. The true b. p. of 100% HNO_3 lies between 85° and 86°. It was found that the concn. of the max. b. p. mixt. decreased regularly from 68.4% HNO_3 at 870 mm. to 65% HNO_3 at 40 mm. Complete tables and graphs give the b. ps., partial pressures and total pressures from 40 mm. to 870 mm. and 40° to 125°. Mixed acid solns. were investigated from 317 mm. to 760 mm. and the results are given in numerous tables and triangular graphs. Reducing the pressure does not affect the shape of the b. p. curves but does lower the values. The lowering amounts to about 25–30° from 760 to 317 mm. Lowering the pressure affects the compn. of the emitted vapors only slightly, the effect being in the direction of an increase in HNO_3 concn. for any given mixt. The compn. of the vapors is almost wholly a function of the H_2O content of the mixt.; thus, mixts. containing less than 20% H_2O give off vapors containing more than 90% HNO_3 when the H_2SO_4 content lies between 3% and 68%, and mixts. containing less than 30% H_2O a vapor of 80% HNO_3 when the H_2SO_4 lies between 15% and 55%, etc. For details the original article must be consulted. In conclusion numerous examples are given of the graphical properties of the triangular system of coördinates and the application of graphical methods in the solution of problems in nitric acid preconcentration, and nitric acid concentration, both in retort and tower. It is pointed out that these graphical methods are applicable to any 3-component system of which 2 components are volatile at the temp. of the expt. F. C. Z.

Lead corrosion with relation to sulfuric acid manufacture. Wm. G. McKellar. *J. Soc. Chem. Ind.* **40**, 137–41T(1921).—As the result of many years' experience the author concludes that many inexplicable failures of so-called chemical lead in H_2SO_4 chamber construction are due, not to the compn. of the Pb, but to strains set up by too rapid rolling of the Pb, or by its method of support in constructing the chamber. Analysis alone tells little of the value of Pb for chem. purposes, but combined with photomicrography can be of great value. Photomicrographic work reveals that Cu does not form an alloy with Pb when Pb predominates, and hence the protective value of Cu is mythical. Cu might be of value in refining the Pb, but it would have to be carefully removed subsequently, as traces present probably set up galvanic couples. Plant experience has shown that Cu-treated Pb so far has shorter life than untreated Pb. All expts. and experience so far still indicate that Pattinsonian Pb is superior to Parkes Pb, and since Zn is insol. in Pb, the presence of any Zn not removed after the sepn. of the Ag would be quite as detrimental as Cu. Moreover, since Zn is not shown up micrographically as readily as Cu it is much likelier to be overlooked. F. C. Z.

The effect of the presence of chlorine on the absorption of nitrous gases. H. W. Webb. *J. Soc. Chem. Ind.* **40**, 162–4T(1921).—Attention is called to the fact that in HNO_3-absorption systems on plants working up Chile nitrate the efficiency of absorption is relatively much greater in those towers where the circulating acid strength is 30–40% HNO_3. In these same towers the rate of decrease of HCl, formed from the NaCl originally in the nitrate, is also greatest. The following explanation is offered: HNO_3 forms two hydrates, $HNO_3.H_2O$ and $HNO_3.3H_2O$, having 77% and 54% HNO_3, resp. Therefore, above 54% HNO_3 no "free" H_2O is present. Hence (as proved by actual expt.) the reaction $HNO_3+3HCl \longrightarrow NOCl+Cl_2+2H_2O$ takes place only with acids above 55–60% HNO_3. The resulting NOCl meets no free H_2O in the first towers, hence the main reaction is the decompn. of the HCl, while the NO_2 present reacts in

the ordinary way, yielding HNO_3 and HNO_2. When the gases meet acid with less than 55–60% HNO_3, however, the following reactions commence: (1) $NOCl+H_2O \longrightarrow HNO_2+HCl$; (2) $Cl_2+H_2O \longrightarrow HClO+HCl$, (3) $HNO_2+HClO \longrightarrow HNO_3+HCl$. The Cl now plays a very important part, *viz.* it oxidizes the HNO_2 formed from the NOCl and accelerates the conversion of NO_2 to HNO_3 by oxidizing also the HNO_2 formed in this reaction. The resulting displacement of the equil. causes a more rapid absorption of NO_2. From the above it follows that the exit gases should contain no free Cl_2, but only NOCl. An actual analysis showed the ratio NO:Cl in the exit to be exactly the same as in NOCl. F. C. Z.

Utilization of bitterns. A. J. TURNER. Dept. of Industry Bombay Presidency, *Bull.* **2**, 14 pp.(1920).—The textile industry of India uses large quantities of $MgCl_2$, the supply of which from Germany was stopped by the war. The use of $CaCl_2$ seemed satisfactory but made no headway. Brines at Kharaghoda were found to contain appreciable amts. of $MgCl_2$; they contain no K or I so that the recovery of the $MgCl_2$ is simple. The first 2 plants erected were primitive, not economical and the product was not comparable to the German material. Production was later put on an improved basis and purification is now effected by holding the $MgCl_2$ crystals at 120° to permit settling out of $MgSO_4.H_2O$. Kharaghoda can supply all of India's needs and export some of the product. Br, estd. at 1800 tons annually, Epsom salt, magnesia cement, Na_2SO_4, HCl, and $ZnCl_2$ are by-products of com. value. G. R. JACKSON

Transformation of hydrogen sulfide to sulfur by activated carbon (ENGELHARDT) **21.** Water hyacinth (potash recovery) (FINLOW) **11D.** Electrifying substances prior to their chemical reaction (U. S. pat. 1,377,553) **4.**

Abhandlungen aus der Braunkohlen und Kali-Industrie. Halle a. S. Wilh. Knapp. M 11.40.

BERL, E.: **Taschenbuch f.r die anorganisch-chemische Grossindustrie.** 6 ed. Berlin: Julius Springer. Berlin: M 64. For review see *Chem. Trade J.* **69**, 95(1921).

Sulfuric acid. G. MIRAT and P. PIPEREAUT. Brit. 163,030, Apr. 13, 1921. The gases from a Glover tower are led to the top of the first of a series of small lead chambers, the gases passing through the series by cooled connecting pipes. The gases enter each chamber at the top and leave near the bottom by a pipe which slopes upwards slightly. The pipe from the Glover tower has a siphon to discharge condensate into the tray of the chamber. The other connecting pipes are of rectangular section with upstanding flanges forming a gutter for cooling-water. The pipes may be wholly immersed in H_2O. The trays at the bottom of the lower chambers are connected together and discharge acid of 52° Bé. to store tanks, and also the trays of the upper chambers which discharge nitrous H_2SO_4 to store tanks; and the acid from the lower chambers is "caused to flow at points within the pipes, whereby a constant movement of acid in the chamber will be obtained"; and "at the upper points, corresponding to the upper chambers, acid at 60–62° Bé. is caused to flow." The gases escaping from an upper chamber are passed through a series of ten small stoneware chambers arranged in the same manner as the Pb chambers. The first four contain H_2O, and the remainder strong H_2SO_4.

Nitrous gases. NORSK HYDRO-ELEKTRISK KVAELSTOFAKTIESELSKAB. Brit. 163,026, Dec. 14, 1920. In the absorption of dil. nitrous gases by means of solid absorption agents, and the decompn. of the resulting product to produce concd. nitrous oxides and HNO_3, the combined process is conducted in retort-like, acid- and fire-proof vessels surrounded by gas-tight jackets capable of resisting comparatively high pressures. The hot gases before actually entering the retorts pass into the space between the jacket

and the retort in order to heat the latter and thus enable either absorption or decompn. to take place. The absorbent may be such as is described in 137,071 consisting of a mixt. of a dry base with one or more metallic oxides and the absorption is advantageously effected at 300–600°. A suitable app. is specified.

Oxidizing ammonia. J. R. PARTINGTON. U. S. 1,378,271, May 17. A mixt. of NH_3, steam and O is preheated and then passed into contact with a catalyst such as Pt gauze to produce N oxides.

Catalytic agents. NITROGEN CORPORATION. Brit. 163,046, May 9, 1921. A catalyst for such reactions as the oxidation of NH_3, MeOH or methane, or for the preferential combustion of CO in presence of H by reaction with steam, is prepd. by heating Ag or CuNCN, or a mixt. of these, in the presence of air to the point where puffing occurs. By incorporating a ferro- or ferricyanide, *e. g.*, Bi ferrocyanide, Bi ferricyanide, Ca Ce ferrocyanide, Ce Co ferrocyanide, V ferrocyanide, or Mo ferrocyanide, with the starting material, an activated product is obtained. The Ag and Cu cyanamides are prepd. by pptg. a dissolved cyanamide with $AgNO_3$ and $CuCl_2$, resp.

Ammonia; ammonium salts; nitrogen; hydrogen. NITROGEN CORPORATION. Brit. 163,047 May 9, 1921. $(NH_4)_2CO_3$ is prepd. by first producing a mixt. of N and H by cracking a gas oil in the presence of air and steam, then catalytically oxidizing the contaminating CO, and finally removing the CO_2 produced with NH_3, which is prepd. by causing the N and H of the mixt. to combine. The $(NH_4)_2CO_3$ may then be transformed into $(NH_4)_2SO_4$. The high-temp. treatment in tubes of refractory material of the gas oil, air and steam, yields a mixt. of N, H, CO_2, CO and H_2O vapor. This mixt. is passed over Fe_2O_3 or other catalyst maintained at a high temp., whereby most of the CO is eliminated by preferential combustion in the presence of such a catalyst as that described in 163,046 (preceding abstr.). CO_2 is removed by treatment with NH_3, prepd. as below and preferably in aq. soln., leaving a mixt. of N and H, in the proportions requisite for NH_3 synthesis provided the starting materials for the cracking operation were suitably proportioned. The H and N of the mixt. are then caused to combine in the known manner under pressure and at high temp. and preferably in presence of a catalyst comprizing a metallic cyanamide or cyanide; the resulting NH_3 is absorbed in H_2O and a desired proportion—in practice, the whole—of the soln. is used for the aforementioned elimination of CO_2. The $(NH_4)_2CO_3$ obtained may be transformed into $(NH_4)_2SO_4$, the CO_2 evolved being collected and liquefied; or the $(NH_4)_2CO_3$ may be converted to $(NH_4)_2SO_3$ by treatment with SO_2, the sulfite being then oxidized to sulfate in any way, say by passing air through its aq. soln. in the presence of a catalyst such as V_2O_5.

Recovery of ammonia. J. H. MACMAHON. U. S. 1,378,593, May 17. NH_3 vapor is recovered from the fixed ammonia present in the feeder liquor of the ammonia-soda process by treating the NH_4Cl in the liquor with Ba sulfide to form NH_4 sulfide and $BaCl_2$, sepg. these salts and reacting upon the NH_4 sulfide with NaOH to liberate NH_3.

Alumina. M. BUCHNER. Brit. 172,303, Nov. 28, 1917. $Al(OH)_3$ is obtained in a granular, easily filterable condition by pptn. of the salt with five or more times the theoretical quantity of NH_4OH soln. or liquid NH_3 or 8 or more times the theoretical quantity of gaseous NH_3. Super-concd. NH_4OH soln. (*i. e.*, soln. obtained under pressure) may be used. Even a dry salt may be thus treated with gaseous NH_3, provided that sufficient H_2O of crystn. is present to produce the hydroxide or sufficient H_2O is supplied with the NH_3 gas.

Ammonium sulfate. S. E. LINDER and R. LESSING. U. S. 1,377,493, May 10. Com. $(NH_4)_2SO_4$ is treated with $Ca(OH)_2$ or other alk. compd. in order to neutralize free acid which it contains and is at the same time agitated and freed from H_2O by tumbling in a drum or ball mill in a current of air.

Decomposing or dissolving feldspar or other difficultly soluble substances with acids. H. D. RANKIN. U. S., 1,378,485, May 17. Magnetite, feldspar or similar material which is resistant to solvents is heated with just sufficient acid, *e. g.*, strong H_2SO_4, thoroughly to wet the material, in a closed vessel, to a temp. sufficient to boil the acid, in order to dissolve or solubilize constituents of the material.

Soluble compounds of potassium from rocks. O. RAVNER. U. S. 1,377,601, May 10. See Can. 201,461 (*C. A.* **14**, 2400).

Potash from brines. G. HECKER. U. S. 1,378,410, May 17. Concd. hot liquors contg. borax and K salts are agitated and rapidly cooled until the K salts are pptd. as coarse crystals of good white color while the borax remains in soln. and the crystals are sepd. from the soln. The method is applicable to the treatment of liquors such as are obtained from natural potassiferous brines.

Barium carbonate. J. H. MACMAHON. U. S. 1,378,595, May 17. The NH_4HCO_3 content of the feeder liquor of the ammonia-soda process is converted into $BaCO_3$ by treating the soln. with $BaCl_2$, the $BaCO_3$ is sepd. from the soln. and the remaining soln. is treated with Ba sulfide to form $BaCl_2$ and the latter is used for the production of additional $BaCO_3$.

Barium chloride. J. H. MACMAHON. U. S. 1,378,594, May 17. NH_4Cl is crystd. from feeder liquor of the ammonia-soda process, these crystals are dissolved and the soln. is treated with Ba sulfide. $BaCl_2$ is crystd. from the soln. thus formed.

Zinc chloride. P. DANCKWARDT. U. S. 1,378,219, May 17. A soln. of $AlCl_3$ is treated with ZnO, the pptd. Al oxide is filtered out of the $ZnCl_2$ soln. and the filtrate is evapd. and the $ZnCl_2$ is fused. Waste $AlCl_3$ from petroleum oil treatment may thus be used for making $ZnCl_2$.

Purifying zinc solutions. S. FIELD and METALS EXTRACTION CORPORATION, Ltd. Brit. 162,030, Dec. 19, 1919. A Zn sulfate or other Zn soln. is freed from foreign metals by treatment in the presence of a Hg salt with a subdivided metal electropositive to the impurities. Zn, Al, and alloys thereof are suitable electropositive metals; they may be powdered or granulated, Zn fume or blue powder being advantageous. The Hg as $HgCl_2$ or $Hg(NO_3)_2$, or, when Zn is to be electrodeposited, as $HgSO_4$, may be added as a soln. or directly dissolved in the Zn soln. before the treatment or at any suitable prior stage. Two lb. of Hg in the form of sulfate, and 40 lb. of Zn, suffice for 10 tons of crude Zn soln. This may be obtained from ore by treatment with spent electrolyte or other soln., and before the purification is brought to an acidity of 0.1–0.2% by means of incomplete neutralization, or by neutralization for the removal of SiO_2, etc., followed by acidification. During the purification the liquid may be heated to 70–100° and gently agitated. Cu, As, Sb, Bi, Cd, Ni, Co, and other metals are pptd. as a sludge, from which Hg can be recovered by distn. or otherwise. Fe may be removed before or after the above purification. If Al is used as the electropositive metal, it may be subsequently removed, but is not injurious in the electrodeposition of Zn. Cf. 138,950 (*C. A.* **14**, 1789).

Recovering water-soluble values from furnace gases. F. S. MOON. U. S. 1,377,363, May 10. Hot furnace gases are passed in contact with a flowing stream of H_2O to dissolve a sol. constituent of the gas such as K compds. and collect suspended material. Tallow, glue or soap or a similar material is added to the liquid to prevent incrustation of the constituents of the liquid on the surface over which it flows, insol. matter is sepd. from the liquid and it is recirculated in contact with additional gas. Sol. constituents are recovered from the soln. when it has attained a sufficient concn.

Refining sulfur. R. F. BACON and C. N. WENRICH. U. S. 1,378,084, May 17. S in pellet form is obtained by maintaining a body of mined S at a temp. of 115–130° and introducing it in the form of drops into cooling liquid such as H_2O containing $CaCl_2$ under such conditions that the drops will solidify.

Casein compositions. E. KRAUSE and B. BLÜCHER. Brit. 162,657, Apr. 29, 1921. Casein is treated with HCHO, dried, and shaped under heat and pressure. The casein may be coarsely or finely ground and moistened with a soln. of HCHO or the unground casein may be soaked in the soln. The drying is preferably continued until no trace of free aldehyde remains. The material is molded at a temp. above 90° and a pressure exceeding 100 atm.

Casein. A. BARTELS. Brit. 162,301, Jan. 16, 1917. In making artificial horn, moist casein, which may be freshly pptd. curd or moistened commercial casein, is treated in kneading or rolling machines or in pug-mills until the layer structure as seen microscopically is completely destroyed. Filling materials may be added before or after this treatment. The product is dried and ground, and on being submitted to high pressure while hot and with a small addition of H_2O yields a transparent mass. Cf. *C. A.* **14**, 212.

Adhesive. J. H. THICKENS. U. S. 1,377,739, May 10. An adhesive adapted for making multi-ply wall-board is formed by mixing Na silicate soln. of about 35° Bé. with about 80% of clay, and allowing the mixt. to stand for about an hr. to permit the clay to absorb Na silicate and form a slowly setting adhesive of high viscosity.

Deflocculating graphite, etc. E. G. ACHESON. Brit. 163,032, Apr. 18, 1921. See *C. A.* **14**, 2535.

Decolorizing-carbon. DEBRUYN, LTD. and C. REVIS. Brit. 162,117, Feb. 6, 1920. A decolorizing-carbon is prepd. from the waste filter-press residues from the refining of edible oils, such as cotton-seed oil or shea-nut oil, by heating them in a reverberatory or similar furnace at a temp. just above the flash-point of the oil they contain, and with restricted admission of air. The product, which is a porous carbonaceous mass, is cooled out of contact with the air, washed with dil. acid to neutralize any alk. salts formed by the incineration of contaminating soaps, and finally pressed into cakes and dried. Lampblack is collected as a combustion product in the flue of the furnaces.

Polishing and sharpening powders. E. M. BOWERS. Brit. 162,161, Apr. 16, 1920. A sharpening and polishing powder is obtained by heating at least to redness a mixt. of say 2 parts of asbestos powder and 1 part of cotton waste or similar carbonaceous matter. Rouge or mineral color may be added.

Cleansing and polishing compositions. M. L. WILLIAMS and J. F. MOSELEY. Brit. 162,691, Oct. 16, 1919. The hydrous aluminium silicate known as bentonite is incorporated with the salts of fatty acids in the manuf. of soaps, polishes, and dressings such as metal, furniture, floor, linoleum, leather and like polishes, dressings, and preservatives.

Impression paper. S. E. SCHUER. U. S. 1,377,368, May 10. Impression paper is formed by coating a carrying sheet of paper with a mixt. of soft soap and soft coal soot.

Printing-plates. E. E. NOVOTNY. U. S. 1,377,501-19, May 10. These 19 pats. relate to the manuf. of printing plates, matrices, and similar articles, from various materials, including phenolic resins, rubber, furfural, Sn-Pb alloy foil and cement.

Resonant diaphragm. A. GELBERT. U. S. 1,377,677, May 10. Diaphragms suitable for phonograph reproducers are formed of hardened gelatin coated with a pyroxylin varnish.

Resinous mixture adapted for forming sound record blanks. T. A. EDISON. U. S. 1,377,192, May 10. A compn. adapted for the manuf. of phonograph records or other molded articles is formed of cotton flock held together by a binder comprizing a resin and a drying oil, *e. g.*, pine resin and oxidized linseed oil, with a filler such as china clay.

Oxidized resin mixture adapted for making sound records. T. A. EDISON. U. S. 1,377,193, May 10. A mixt. suitable for making phonograph records or other molded

articles is formed from a finely divided filler, *e. g.*, china clay and cotton flock held together by a binder comprizing oil and oxidized pine resin or a similar oxidized resin.

Resurfacing phonograph records. E. T. HAILS. U. S. 1,378,344, May 17. Phonograph cylinders are resurfaced by first obliterating the record trace by wiping the record with a solvent such as kerosene and then wiping the record with a mixt. of alc., ether and vinegar.

Composition for stopping leaks. M. G. RAY. U. S. 1,377,275, May 10. A mixt. for stopping leaks in automobile radiators is formed of Al 1, graphite 1, flaxseed meal 1, "washing soda" 0.5 and "lye" 2 parts.

Shoe last. O. C. WINESTOCK. U. S. 1,377,241, May 10. Shoe lasts are formed of wood impregnated with rubber.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Dental ceramics: a treatise on the technic of porcelain manipulation. FRED R. FELCHER. *Dental Cosmos* **63**, 387–94, 483–8, 624–32, 681–7(1921).—A comprehensive survey of the entire field. JOSEPH S. HEPBURN

The clays of the Tandil Mts., Argentine Republic. M. A. ZAMBONI. *Anales soc. quim. Argentina* **8**, 190–9(1920).—Complete phys. and chem. analyses of several clays are given. L. E. GILSON

Enameled brick. G. BRIFFE. *Rev. mat. constr. trav. pub.* **141**, 87–90B(1921).—A simple layout for a small enameled brick plant to produce 350,000 brick annually. No details. LOUIS NAVIAS

One solution of the porcelain insulator problem. E. E. F. CREIGHTON AND F. L. HUNT. *Elec. Rev.* **79**, 17–20(1921); *J. Am. Inst. Elec. Eng.* **40**, 480–2(1921).—Failure in cemented porcelain insulators is prevented by arresting the expansion of the cement used, through removal of the moisture when it is thoroughly set and preventing the moisture from re-entering it and causing repeated expansions. This is done by impregnating the cement after it has set with a pitch under vacuum and heat treatment. Small pieces so treated can be soaked in H_2O for days without showing absorption. Insulators thus prepd. have been installed on a 66,000-volt transmission line near the seashore for 3 years without a single failure occurring. L. C. KRUEGER

The siliceous rocks considered from the viewpoint of manufacture of silica bricks. L. BERTRAND AND A. LANQUINE. *Bull. offic. direc. recherch. sci. ind.* Nos. 1 and 2, **1919**, 121–7; *Rev. géol.* **1**, 408–10(1920).—A discussion of the effect of the amt., nature, and mode of distribution of impurities in SiO_2 rocks on their use for making SiO_2 brick. E. T. WHERRY

Carborundum refractories in heat-treating furnaces. M. L. HARTMAN. *Trans. Am. Soc. Steel Treating* **1**, 601–3(1921).—In addition to superior resistance at high temps., the elimination of extensive repairs compensates for a higher initial cost when carborundum is used. W. A. MUDGE

Bricks; pottery. C. W. WALLACE. Brit. 162,483, March 11, 1920. Bricks, pottery, and artificial stone products are obtained from clayey material, *e. g.*, as the white clayey material found near Molo in British East Africa, by introducing pressed, turned, or otherwise shaped, or unshaped pieces of the clay directly into the flames of a furnace, heating throughout, and effecting sudden cooling by plunging into H_2O, etc.

"Antislipping" vitrified tile. M. F. BEECHER. U. S. 1,377,957, May 10. A

ceramic "safety tread" is formed with a rough tread surface of durable, wear-resisting vitrified non-glassy clay material, with granular material, such as cryst. Al_2O_3 forming a considerable portion of the surface.

"Antislipping tile." H. K. DODGE. U. S. 1,377,960, May 10. Tread blocks are formed of particles of cryst. Al_2O_3 or material of similar hardness constituting the major portion of the block, and a binder of vitrified ceramic material.

Kiln-lining. A. F. MEYERHOFER. U. S. 1,378,710, May 17. See Can. 209,766 (*C. A.* **15**, 1175).

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

The addition of trass to cement. C. PLATZMANN. *Zement* **9**, 227–8(1920); *Chimie & industrie* **5**, 317(1921).—Tests carried out on mixts. of 1 part by wt. of cement, 0.5–1 part of trass, and 4, 6, 8, and 11 parts of gravel led to the following conclusions: trass may be added to the mixt. to economize cement, its physical and chem. properties being suitable for the purpose. Cement-trass-gravel concretes were stronger than cement-gravel concretes having the same cement content, owing to the fineness of the trass. From an economic point of view, concretes to which trass has been added are not more expensive than those which do not contain any. A. P.-C.

Special high resistance portland cements. ENDELL. *Zement* **9**, 25–8(1920); *Chimie & Industrie* **5**, 317(1921).—E. gives the results obtained in the course of tests of special German and Austrian cements which had a remarkably high strength at the end of 2 days, tensile 10 kg. and compressive 180 kg. [per sq. mm. ABSTR.]. Such results are of no great practical importance. Müller Rüdersdorf, in the course of the testing of several hundred samples of com. cements, found the following values at the end of 28 days: 8% below 300 kg., 14% 300–50 kg., 26% 350–400 kg., 15% 400–50 kg., 22% 450–500 kg., and 15% 550–600 kg. The strength requirements at present in force are sufficient for all purposes. The production of special cements is easily obtained by adding more CaO, but this entails 2 drawbacks: getting too near the limit where expansion is liable to occur, and greater fuel consumption for burning. These are scarcely compensated by the possibility of removing the forms from the reinforced concrete work at the end of 2 days. A. P.-C.

The behavior of cement mortars in sulfate-bearing waters. H. NITZCHE. *Zement* **9**, 37–40, 50–3(1920); *Chimie & industrie* **5**, 317(1921).—As a result of serious troubles encountered with concrete work carried out in the neighborhood of Frankfort, where there is a subterranean sheet of sulfate-bearing water, N. carried out numerous tests in which local contractors were interested. Two large tables give a summary of the results obtained on concretes having varying amts. of portland cement and of slag cement immersed in pure and in sulfate-bearing waters during 1, 2, and 3 yrs. Numerous photographs are given of the test pieces thus treated. Cf. *C. A.* **14**, 606. A. P.-C.

Experiments with blast-furnace slag. H. BURCHARTZ. *Stahl u. Eisen* **41**, 193–200 (1921).—The following conclusions regarding the use of blast-furnace slag in *cement* are drawn. The resistance of reinforced concrete to sea water is dependent on the density of the cement. Cement from blast-furnace slag made in the following proportions 1 pt. cement, 2 pts. fine slag, 3 pts. coarse gravel is as good as silica cement. Cf. *C. A.* **14**, 3143. R. S. DEAN

The dependence of the lime industry upon nature and science. A. D. LITTLE. *Chem. Met. Eng.* **25**, 149–52(1921).—An address. The markets for lime developed as a result of scientific investigation. The technical problems of the industry are discussed. Phys. properties are often more important than chem. properties. Progress already

attained in kiln design and the mechanical equipment for the transportation of materials must be followed by accurate chem. control of operations. W. H. BOYNTON

The slaking of lime. KOSMANN. *Verh. Ver. Beförd. Gewerfleiss.* No. 5, 61–5 (May 1920); *Chimie & industrie* **5**, 317(1921).—The paste resulting from the interaction of CaO and H_2O during slaking and from the transformation of the $Ca(OH)_2$ to the colloidal state is due to the formation of a gel of Ca tetrahydrate (64%) and of a sol of lime water (36%) contg. 4.572% of CaO. A. P.-C

Artificial paving blocks. J. KLINKMÜLLER. *Verh. Ver. Beförd. Gewerbfleiss.* **3**, 69–96(1920); *Chimie & industrie* **5**, 64(1921).—Review of the various materials proposed in Germany for the prepn. of paving blocks and of a series of patents relative to the use of cement or asphalt concretes, with or without reinforcing. A. P.-C.

Slaked lime and milk of lime (KOSMANN) (KOHLSCHÜTTER) **6.**

Concrete bricks. W. W. CRAWFORD. Brit. 162,683, Dec. 1, 1919. In the manuf. of bricks, building blocks, etc., common earth, soil, clay, etc., are burnt in an oxidizing atm. at a temp. of about 1500°, *e.g.*, in a furnace having oil burners, as described in 2860, 1915. The burnt material is mixed with a relatively small quantity of portland or like cement previously dehydrated, preferably at about 130°, moistened with preferably warm H_2O and molded under pressure preferably at least 150 lbs. per sq. in. The blocks are then immersed in cold H_2O for several hrs. and air-dried at a temp. slightly above freezing point.

Artificial stone; concrete. E. C. BAYER. Brit. 162,318, Nov. 17, 1919. Diatomaceous earth is mixed with feldspar or other siliceous mineral and the mixt. is heated to about 1200–1300° until the feldspar is fused or softened and forms a coating round the particles of diatomaceous earth. The materials may be mixed with a little H_2O and formed into small pieces or into a block which is broken up after being heated. The product forms a light aggregate for concrete and may be used as a heat-insulating compn.

Burning lime. J. C. SCHAFFER. U. S. 1,377,367, May 10. A steam supply is provided by which steam may be introduced beneath the grate of the furnace which heats a lime-burning kiln, in order to humidify the heating action of the furnace and temper the combustion zone extending from the furnace into the kiln.

Producing lime. W. CROW and J. C. SCHAFFER. U. S. 1,377,401, May 10. Limestone is mixed with hydrated lime and the mixt. is gradually heated for effecting porous nodulization. The product thus formed is suitable for making mortar or wall coatings.

Floor-covering. J. J. TOMEC. U. S. 1,378,498, May 17. A floor-covering is formed of a lower layer of asphaltic material reinforced with reticulated metal and an upper layer of linoleum.

Floor-coverings. M. ROBERTS. Brit. 162,514, Apr. 6, 1920. A jointless floor covering is made by mixing calcined magnesite with an equal wt. of sawdust, cork dust, or wood pulp moistened with $MgCl_2$ soln. adding 5–10% of French Chalk and 12½% of coloring matter, and subsequently adding $MgCl_2$ soln. at 28° Bé. till the desired plasticity is obtained. The coloring matter may be omitted. According to the provisional specification, asbestos may also be used as an ingredient.

Cork board. R. M. S. CASSANO. Brit. 162,645, Apr. 6, 1921. Cork slabs or blocks are produced by heating finely divided cork in small quantities, preferably in a rotating drum, until the resinous constituents of the cork are sufficiently exuded, then passing the cork into molds and compressing it. The gases evolved during the heating may be utilized in the furnaces, or separately collected.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Work of the commission for utilization of fuels. WALCKENAER, CORNU-THENARD AND METAYR. *Rev. metal.* **17**, 757–64(1920).—See *C. A.* **15**, 1385. J. L. WILEY

Grading and classification of coal. W. J. WYDERGH. *S. African J. Ind.; Iron and Coal Trades Rev.* **103**, 36(1921).—W. criticizes the principal systems used for classifying coals, such as calorific value, fuel ratio as used by the Penn. Geol. Surv., C:H ratio as used by the U. S. Geol. Surv., Seyler's classification, Bone's classification, etc., in that they are too limited in scope, complicated, and subject to errors. The difficulty is to devize a universally acceptable method, which will correctly and adequately reflect the practical value of the coal simultaneously for all industrial purposes. Such a matter should be decided by a committee of experts. The suggestion is put forward that while calorific value should continue to be the main basis of classification, it should be accompanied either by a statement of the C:H ratio or by a descriptive classification on the lines adopted by Bone (Coal and Its Scientific Uses, 1918). J. L. WILEY

Trent process of cleaning coal. G. ST. J. PERROTT AND S. P. KINNEY. Bur. Mines, *Repts. of Investigations* **2263**, 18 pp.(1921); *Am. Gas. J.* **115**, 143–4, 148–53 (1921).—The Bur. of Mines has investigated the Trent process for producing an efficient fuel from mixed coal and oil. Results were favorable, the fuel produced being 95% combustible. Special value of the process is removal of ash, or non-combustible mineral matter, from low-grade coal. Amt. of ash removed in the tests ranged from 30 to 75%. S reduction is fairly good in the case of anthracite coals but low in the case of bituminous coals. Results point to the desirability of preliminary water concn. of high-S coals for removal of pyrite before treatment by the Trent process. It has not been found feasible to treat lignites without preliminary carbonization owing to the difficulty of forming a coherent agglomerate of the raw lignite and oil. The process consists in first grinding the coal, ridding it of extraneous mineral matter, then mixing with water and oil, and churning the mixt. until a pasty mass, made up of small egg-shaped granules known as amalgam, is formed, then washing with water. Pulverization to 200 mesh is generally the most satisfactory fineness. Any oil of proper viscosity, 135 sec. Saybolt, can be employed, about 30% in wt. of the coal. Using an oil which distils at lower temp. than the coal makes possible the reclaiming of the oil and results in a powdered fuel. Use of a heavy oil contg. pitch produces a coking product after distn. although the coal used may be non-coking. Oil losses in the refuse or water are practically negligible. Com. possibilities are broad. Flue dust can thus be converted into coke, graphite ore sepd. from its gang and gas-tar emulsions can be dehydrated by mixing with powdered coal, the amalgam being retorted for further gas-making. Probably the greatest advantage lies in the ability to utilize low-grade coals by removal of the large proportions of ash. Amalgam from which the oil is not distd. can be handled readily or forced through pipes and can be stored under water without detriment. J. L. W.

The determination of volatile matter in coal. ACHILLE DELCLÈVE. Société des Houillères de Saint-Etienne. *Chimie & industrie* **6**, 33–40(1921).—The phenomena involved in the detn. of the volatile matter of coal is investigated from a theoretical and exptl. point of view, and it is shown that the detn. is not accurate as a means of grading coals. The % of volatile matter on the ash-free basis can at best serve as a rough method of grading, provided the ash-content is low. The objections to the method are based on the fact that the inorg. impurities in the coal are affected by the heating and lose in wt. to a considerable extent, and also the CO_2 given off reacts with the fixed C ($CO_2 + C = 2\,CO$) reducing the amt. of the latter. The method has been chosen for the classification of coals on account of its rapidity and simplicity; and it is suggested

that a correction coeff. be detd. according to the amt. and nature of the ash. Also in *Chem. Met. Eng.* **25**, 182–86(1921). A. P.-C.

Preliminary study of the varieties of coal found in the Argentine Republic. PEDRO LANDEIRA. *Anales soc. quim. Argentina* **8**, 200–12(1920).—Lignite and low-grade bituminous coal predominate. It is believed that better grades will be found at greater depths. L. E. GILSON

The coal deposits of Marayes, San Juan, Argentine Republic. MIGUEL PATTIN. *Anales soc. quim. Argentina* **9**, 54–65(1921).—The deposits are extensive but of poor quality. L. E. GILSON

The production of oils by hydrogenation of coal. I. The hydrogenation of coal and other solid fuels by means of sodium formate. FRANZ FISCHER AND HANS SCHRADER. Mülheim-Ruhr. *Brennstoff Chem.* **2**, 161–73(1921); cf. *C. A.* **10**, 1926, 2398, 2401; **11**, 206; **12**, 760; **13**, 2989; **14**, 818, 2414.—Reduction expts. were carried out with coal, lignite peat, wood, lignin and cellulose, the major part of the work being with a Rhenish brown coal of 16.3% H_2O and 4.6% ash content; dry-basis analysis, 62.5% C, 4.7% H. The first series was at ordinary pressure, with an Al coking app. The temp. was raised to 400° in $^3/_4$ hr., and held there for 3 hrs. The av. tar yield when the coal was heated alone was about 7% and the residue 58%, regardless of whether H, N or steam was used as the inert gas. A mixt. of 1 part of coal with 4 of HCOONa, made by evapg. a suspension of the coal in the salt soln. and drying at 105°, was similarly heated; the tar yield (based on the coal) rose to 22–27%, according to the nature of the inert gas used, about 80% of a solid residue remaining in the retort. The presence of a small amt. of O decreased the tar yield markedly. The next series of expts. was made in a small steel autoclave of about 31 cc. capacity. Coal heated alone in this app. to 400° for 3 hrs. gave an Et_2O ext. of 1.3% as against 1.6% in the original coal; the addition of twice its wt. of water raised the yield to 10.1%. The addition of twice its wt. of dry NaCOOH brought the yield of Et_2O ext. to 44%, and adding an equal wt. of H_2O raised this only 0.9% further. The ext. isolated was a reddish brown salve, smelling like tar. Similar expts. with temps. of 350° and 450° instead of 400° resulted in yields of 28.8% and 7.9% resp., so that 400° seemed to be near the optimum temp. When the coal-formate ratio was decreased to 1–2 instead of 1–4, the yield fell to 26.6%, while with a ratio of 1–8 it rose to 48.4%. In the latter case the residue contained only 11% of the original coal. A whole series of fuels was then treated, in the proportions found best, *viz.*, 1 part of the fuel, 2 parts dry NaCOOH, 2 parts water, heated for 3 hrs. at 400° in the autoclave. The yields of Et_2O-ext. and residue are referred to dry, ash-free substance. The % Et_2O ext. and % org. residue, resp., were: Half-coke (gas coal) 9.8, 74.5; anthracite 1.6, 95.5; "lean" coal, Roland mine 10.7, 74.7; "fat" coal, Osterfeld mine 9.2, 68.7; gas coal, Lohberg mine 39.2, 46.9; spontaneously combustible fat coal, Radbod mine 26.3, 51.5; cannel coal 28.2, 22.3; half coke (from lignite) 32.4, 36.7; Saxon lignite 43.4, 4.9; Rosenthal lignite 36.3, 5.5; Rhenish brown coal 45.0, 6.6; lignite from Zittau 26.8, 10.2; humic acid (from lignite) 37.1, 4.7; peat 24.2, 4.7; charcoal 5.9, 79.7; birch wood 19.6, 2.2; fir wood 19.5, 2.5; lignin 22.3, 35.4; cellulose 12.9, 3.2; cane sugar 17.3, —. The character of the isolated ext. varied from a solid resin produced from the anthracite to a thin, brown oil of ethereal odor from the cellulose. The residues varied considerably as to their soly. in C_5H_5N, without any regularity being obvious in the series. The yield of Et_2O ext. appears to depend not upon the bitumen content of the fuel, but upon the presence of the phenols characteristic of lignin and humic acids; the elementary analysis of several of the exts. averaged about 85% C, 8% H. Further expts. were carried out with an autoclave of 116 cc. capacity. A dry mixt. of the brown coal with about twice its wt. of HCOONa gave 51.3% Et_2O-sol. or 49.5% C_6H_6-sol. ext., and the organic residue was partly sol. in EtOH, completely in

C_5H_5N. The brown C_6H_6 soln. was fairly well decolorized by agitation with a little concd. H_2SO_4. An expt. with H_2O present gave 8.28 l. of gas from 20 g. of coal; the gas contained 39% CO_2 and small quantities of condensible hydrocarbons, some of them apparently aliphatic. The Et_2O ext. was more than $^2/_3$ distillable at ordinary pressure without much decompn., about 50% boiling between 300° and 350°; in fact, it was possible to recover about the same quantity of tar by dry distn. of a reduced product as by Et_2O extn. The final series was comparable to the previous one except that 91.5% HCO_2Na was used instead of the pure salt. The best yield was about $^1/_3$ less than in that case, probably because the coal layer was more than 50% deeper in the autoclave. W. B. V.

Hydrogenated compounds, and their application as fuels for internal-combustion engines. SCHRAUTH. Berlin-Rodleben. *Brennstoff Chem.* **2**, 184(1921).—Author's abstract. Mixts. of tetralin with gasoline or benzene may be used without difficulty as fuel for ordinary gasoline engines; tetralin itself is a suitable fuel for the modern high-compression engine. The higher cyclohexanols produced by hydrogenation of tar phenols may be dehydrated to cyclohexenes, which with cyclohexane and dekalin offer further motor fuel possibilities. W. B. V.

Innovations in firing apparatus for solid fuels. PRADEL. *Feuerungstechnik* **9**, 65–9(1921).—The burning of inferior fuels without mechanical aid is usually accomplished in so-called "free-fall" ovens. P. discusses several types. H. C. PARISH

Organization in the gas industry. ARTHUR DUCKHAM. *Gas J.* **155**, 154–5(1921).—An address. D. shows the need for reorganization and coördination of the various branches of the gas industry. He even would form a British Gas Assoc. and have all the present existing bodies subordinate to it with representatives on the Council from each organization and of equal standing. This would tend to promote harmony, strength and a high grade of work. J. L. WILEY

Economic significance of the gas industry of today. W. BERTELSMANN. *Gas und Wasserfach* **64**, 398–401(1921).—The privations that the German gas industry has been forced to undergo have really been a help to its development. The severe lack of coal has been made up by the utilization of poor grades, lignite, peat, etc. by methods untried to any considerable extent before the war, such as steaming of retorts, manuf. of producer gas, double-gas, tri-gas, etc. Today gas of 3750 to 4000 cal. is giving better service than the former gas of 5000 cal., both for heating and lighting, and at a lower cost. This is brought about in large part by the use of correct appliances and their proper regulation for consuming a lower-grade gas. J. L. WILEY

Determination of benzene hydrocarbons in illuminating and coke oven gas. E. BERL AND K. ANDRESS. *Z. angew. Chem.* **34**, Aufsatzteil, 278–9(1921); cf. *C. A.* **15**, 2167.—The vapor pressure of benzene dissolved in paraffin oil was detd. for 0° and 20°. The vapor pressure of benzene in paraffin oil has a high temp. coeff. so that with a normal benzene content of 20 g. per cu. m. the max. absorption capacity of paraffin oil at 0° with 3.4% by wt. is about 2.7 times as large as at 20°. Activated charcoal can be charged at 20° with 31% by wt. under like conditions. The temp. coeff. of benzene absorption by activated charcoal is relatively low. At 0° it takes up 1.2 times as much as at 20°. The method with the use of activated charcoal for detn. of benzene in gas is essentially more simple, quicker and more reliable to carry out than the paraffin method and gives the benzene hydrocarbons present as such while by the paraffin method this is usually detd. only by weighing. J. L. WILEY

The determination of tar, dust and water in generator gas. E. JENKNER. *Stahl u. Eisen* **41**, 181–3(1921).—The tar and dust are pptd. in a hot tube filled with small glass tubes; the water and some of the tar pass through to a similar cold tube where the remainder of the tar precipitates, the water is absorbed in $CaCl_2$. Details are given. R. S. DEAN

Valuation of combustible gases on the therm basis. NORTON H. HUMPHRYS. *Gas J.* **155,** 33–4(1921).—Sample figures are shown, based on the composition of 5 different gases, for working out details of values for any gas. J. L. WILEY

Fifth report of the research sub-committee of the gas investigation committee of the Institution of Gas Engineers. Simmance recording calorimeter. JAMES W. WOOD. *Gas J.* **154,** 677–84, 744–50; **155,** 35–40, 101–3(1921); 12 figs.; cf. *C. A.* **12,** 546; **15,** 1610.—Results of extended expts. and calcns. under working conditions of the Simmance continuous recording calorimeter. During 9 months' tests, the results agree very closely with those from the Junkers and Boys calorimeters. For control of gas manuf., for large consumers of gas, and for research purposes, where daily adjustment and inspection can be made, it is likely to prove a valuable instrument. Under such conditions the record may be relied upon to within ±1 to 1.5% over 24 hr. For longer periods and general conditions of use, no definite statement is possible. The *Beasley Recorder* also is described. It is a useful instrument for the control of gas manuf. but, from some errors to which it is liable, unsuitable for official purposes. J. L. WILEY

Methods for measuring large volumes of gas, especially applicable to gas plants or coke ovens. C. BERTHELOT. *Rev. metal.* **17,** 668–76(1920).—B. describes briefly, giving advantages and disadvantages, the methods for measurement by means of a gasometer, by the Pitot tube, by the Lecocq method which is based upon the detn. of the exact. vol. of air admitted to the furnace for combustion of the gas, of the vol. of gas drawn out by the exhauster, of the NH_3 in the gas and in the wash water, and at some length, the Murgue method which is based upon the measurement of the loss in pressure caused by a diaphragm inserted in the gas main, the difference in pressure on the opposite sides of the diaphragm being measured by a manometer. The app. is very exact, measuring variations within 0.01 mm. J. L. WILEY

Gas flow measurement. NOAH D. LAMBERT. *Am. Gas. J.* **115,** 93–7, 105–10 (1921); 12 figs.—A discussion of the various methods that are recognized as standard in the measurement of gas. Gas meters are classified in 4 ways: (1) method of showing measurement; indicating, recording and integrating or any combination of these; (2) capacity for measuring; (3) precision; (4) type, as volume, velocity and heat capacity. The principles of various examples of these 3 types are discussed. J. L. WILEY

Automatic regulation of pressure of town gas. C. FRERE. Soc. Tech. du Gaz. *Gas J.* **155,** 99–100(1921); 1 fig.—Modifications made to an app. previously described (*J. Gas. Lighting* **91,** 177–8(1905)) are shown. It insures const. pressure throughout the system of gas mains whatever be the variation in consumption. J. L. WILEY

Natural gas burners improved. I. V. BRUMBAUGH AND G. B. SHAWN. *Gas Age* **47,** 535–40; **48,** 30–37, 73–84(1921); 35 figs.—Investigation was made by the Bureau of Standards on the design and efficiency of natural gas burners. Need of burner improvements is shown and the method of tests is described. The investigation shows that domestic appliances are usually very inefficient, and that the efficiency and quality of the service can be much improved by proper design of burners and correct method of operation. Closed-top stoves, except for room heating, were found to be only 6–13% efficient. With the solid top removed and the utensil placed close to the burner (about 1 inch without allowing the blue inner cone to touch the utensil) the efficiency averages about 45%; the rate of heating is about doubled and the gas consumption decreased about 50%. As soon as the boiling temp. is attained in heating a liquid, the vol. of flame should be reduced to a point that will just maintain the boiling, thus saving gas. To insure good service, the burners should have about 0.08 to 1.0 sq. in. port area for each 1000 B. t. u. consumed per hr. and the area of the throat of the injecting tube should be about 43% of the total area of the burner ports. If above conditions are fulfilled, a standard burner should never consume more than 8500 B. t. u. or 8 cu. ft. per hr. CO and CH_2O are

produced if the inner blue cone of the flame is allowed to touch the utensil. A yellow-flame will produce CO at a rate greater than a blue flame. Increasing the air-gas ratio from 3–1 to 7–1 decreased the rate of formation of CO by approx. one-half. Room heaters or other appliances consuming a very large vol. of gas should always have flue connections. J. L. WILEY

Automatic long-distance gas-pressure recorder. F. GREINEDER. *Gas und Wasserfach* **64**, 261–3(1921).—A detailed description with diagrams of the *Bamag* pressure recorder is given. J. L. WILEY

Automatic safety gas cut-off. A. GREBEL. Soc. Tech. du Gaz. *Gas J.* **155**, 99(1921); 4 figs.—The app. described is a safety device for attachment particularly to the meter for cutting off automatically the supply of gas when the pressure fails or when a break in the connections occurs. It works on the hydrostatic principle of the filling and emptying of a syphon similar to those used in CO_2 recorders. The trapping liquid consists of water containing 20% of glycerol. It is simple in operation and does not get out of order easily. J. L. WILEY

Gas quality and lighting efficiency. E. TERRES AND H. STRAUBE. *Gas und Wasserfach* **64**, 309–14, 329–36, 348–54(1921).—An investigation was made of the lighting efficiencies of both upright and inverted incandescent gas burners with straight coal gas and mixts. of it with 10, 20, 30 and 40% of water gas, producer gas, lignite gas, waste gases with 20% CO_2 and 80% N, and with air, at pressures of 30, 40, 50 and 60 mm. water column. The compn. and sp. gr. of the various gases used are given and the amt. of primary aeration. The effect of the sp. gr. and the pressure upon the amt. of primary aeration is discussed and the effect of this primary aeration upon the mean horizontal candle power of the upright burner. It was found that the lighting efficiency of the upright burner is decreased when the other gases are mixed with straight coal gas, the best results being obtained from the water-gas mixt., followed by that of the lignite-gas mixt., when equal amts. of each of the diluents were employed. If the comparison is made on the basis of the inert gases CO_2 and N, it is found that the N content influences the light intensity to a lesser degree than the CO_2, and, therefore, in specifying the degree of diln. of coal gas with gases of lower calorific power, it is well to state the max. % of CO_2 which can be allowed; N can be present in larger amts. Generally, in the case of the inverted burner, the lighting efficiency increases with the increase in the amt. of primary aeration. Changes in the gas quality are of secondary importance. With mixts. of water gas, the relation is quite different from that for other mixts. With water gas the candle power increases as the % of it in the mixt. increases, the same amt. of primary aeration being considered. With all other gas mixts. the relations are reversed. In respect to absolute lighting efficiency, the inverted burner is much less changeable than the upright burner. According to the degree of primary aeration and the gas pressure employed with all the gas mixts., the candle power ranged between 60 and 110 Hefner candles. Neither the calorific value, between the limits investigated of 3400 to 5500 cal. per cu. m., nor the sp. gr. nor the limits of temp. offer any criterion for judging of the efficiency in the use of gases. It is the degree of primary aeration together with the flame volume that dets. the lighting efficiency of a gas mixt. Flame temps. vary so little between the different gases, that they can be considered as the same for all of them. *Ibid* 440–6.—Investigation was made of flame vol. in upright and inverted burners, and its dependence upon gas pressure and primary aeration, as well as the influence of gas pressure upon primary aeration. The space inside and outside the mantle was divided into zones and samples of the gases in these zones were taken and analyzed. By this means it was detd. that an increase in the gas pressure tends to decrease the flame vol., and that the more complete the combustion at the mantle surface and the higher the temp. at that point, the greater the lighting efficiency. In

the case of the upright burner with straight coal gas and with increasing gas pressure, an increase in the lighting efficiency is obtained in contrast with the other gases. The investigation showed that with lower pressures the vol. of the flame is greater than that of the mantle and that with increase of pressure it more nearly approaches the limits of the mantle, the same increasing the light efficiency. With the coal gas mixts. the flame vol. becomes smaller with increasing pressure and the flame zone withdraws more and more within the mantle surface with resulting diminution in the lighting efficiency. Similar results are obtained by increasing the primary aeration. A further examn. of the combustion both inside and outside the mantle of the upright burner showed that the combustion, begun at the inner cone, continues to take place, and that the secondary air penetrates to a depth of 10 mm. into the mantle. Outside the mantle free O is present and at 1 mm. beyond the surface the combustion is practically complete, and thereafter diln. of the combustion products with secondary air takes place very rapidly. Above the mantle also this diln. of the combustion products continues rapidly. The secondary aeration has also an influence on the lighting efficiency. If primary aeration is cut down, the entrance of secondary air to the hot gases within the mantle furthers the combustion, increases the flame temp. and then raises the lighting efficiency. If primary aeration is complete, the secondary air produces a cooling effect and thus reduces the lighting efficiency. In the case of inverted burners, the relation is more simple, since the shape of the flame is governed by the mantle, and the flame volume and the completion of combustion play the same role in respect to the lighting efficiency as in the case of the upright burner, and in fact the effect of this completion of combustion at the mantle surface is even more marked. No clear relation could be detd. between the lighting efficiencies of the gas mixts. used and the velocities of their combustion. J. L. WILEY

The incandescent gas mantle and the war. GEISEL. *Electrotech. Z.* **24**, 656–7 (1921).—The German mantle mfrs. before the war had depended on foreign sources for their raw materials, *viz.*, ramie thread from Chinese ramie grass, Th and Ce nitrates from Brazilian monazite and asbestos, camphor and castor oil from other countries. Monazite stocks at the beginning of the war fortunately were sufficient for at least a decade. Ramie thread was scarce, however, and artificial silk being confiscated during the war, paper thread was used entirely as a substitute. The difficulties connected with the weaving of a fabric from short staple paper were very great, particularly when the paper was nearly ashless as was essential for this purpose. The candle power of even pure paper mantles was only 60–70% of that of ramie mantles. Mantles of the upright type had originally been strengthened in the head by a structure of woven asbestos. This was replaced by crepe paper, and iron wire was then used for sewing the mantle tops. This gave good durability, because through the scarcity of coal the heat value of the gas was reduced and a shorter flame produced, thus leaving the iron wire out of the range of high temp. As a substitute for the asbestos thread in mantles of the inverted type, the mantle was attached to the magnesia ring by means of a ceramic enamel fixing the mantle rigidly thereto. Condensed phenols were used largely as substitutes for camphor and castor oil in the prepn. of mantle collodions, the latter being required for military purposes. H. S. MINER

Woodall-Duckham chamber ovens for continuous gasification. HEINRICH LININGER. *Z. Ver. Gas- Wasserfach* **61**, 41–3, 55–8(1921).—The ovens are described in detail as is also the water-cooled coke discharger which delivers the coke in an intact, dry state with a temp. of 40–50°. The advantages are as follows: (1) the gasification is carried out under the most ideal and uniform conditions; (2) the yield of tar is about 15% and of NH_3 10% more than with horizontal ovens; (3) the gas, having only a short contact with heated surfaces, is almost free from naphthalene and S; (4) the coke is

of excellent condition, completely dried and cooled and practically devoid of breeze; (5) fuel consumption is very low, loss in the coke is nil and radiation is at a minimum; (6) the ovens are always closed during operation, the charging being done into a holder separate from the retorting space, consequently there are no losses of gas or trouble with smoke; (7) long ascension pipes are avoided, stoppages from tar and pitch are rare; (8) labor requirements are small; (9) the construction is simple, strong and gas-tight, and cost as well as upkeep is low. J. L. WILEY

Economy in vertical-oven operation at the Mödling Gasworks. H. BROOK. *Z. Ver. Gas-Wasserfach* **61**, 52–5(1921).—Operation of the Dessau type of oven is described. With steaming from 1 to 1.5 hrs., 350–360 cu. m. of gas per ton of coal are produced; calorific value 4800–5000 cal. Firing consumes about 15–16% of the gasified coal. The yield of tar is about 55 kg. and of NH_3 2.6 kg. per ton of coal. Labor requirements are small and repairs low. J. L. WILEY

The lignite by-product gas producer. CURT BUBE. Halle. *Brennstoff Chem.* **2**, 186–7(1921); *Z. angew. Chem.* **34**, Aufsatzteil, 314–20(1921).—A brief statement of modern requirements in German producer design. The problem of removing all the tar formed is complicated by the filtering action of the moist fuel in the drying zone; and yet this filtering action is desirable as removing coke breeze from the gas. Slag formation and ash handling, regulation of water vapor or flue gas input, and good air distribution are still partly unsolved problems. In the discussion following the presentation of the paper (*Ver. deutsch. Chem.*, Stuttgart) the view prevailed that it is more important to produce good gas than to recover the highest quality or quantity of tar. W. B. V.

The transformation of hydrogen sulfide to sulfur by means of activated carbon.—a new process of sulfur recovery and gas purification. A. ENGELHARDT. Wiesdorf. *Brennstoff Chem.* **2**, 186(1921); *Z. angew Chem.* **34**, Aufsatzteil, 293–5(1921); cf. *C. A.* **13**, 2436, 3288; **15**, 715.—A brief abstract of a paper delivered before the Ver. deut. Chem., describing a process recently patented by Fried. Bayer & Co. In an editor's note the following information is added. The raw gas is cooled, the tar, NH_3 and $C_{10}H_8$ are sepd., and a small proportion of air is added. The air-gas mixt. passes through a tower of activated C of about 150 mm. of H_2O resistance. Incomplete sepn. of tar from the gas rapidly destroys the activity of the C. In favorable circumstances the C may take up its own weight of S. At regular intervals the charge is removed from the tower and the S extd., best with C_6H_5Cl, which leaves about 8% S in the C. The extd. material is blown with high-pressure steam, cooled in a gas stream, and reused. Also *Gas Age-Record* **48**, 275–9(1921). W. B. V.

Utilization of spent oxide from gas works. P. WAGUET. Inst. Agr. Intern. Beauvais. *Rev. prod. chim.* **24**, 397–404(1921).—Outline of the compn. of spent oxide, of the methods of extg. S, and of prepg. $(NH_4)_2SO_4$, $K_4Fe(CN)_6$, KCN, and Prussian blue, and also of the advantages and limitations of its use as a fertilizer, for destroying weeds, and as an insecticide. A. P.-C.

Absorption of benzene vapors by wood charcoal. ANON. *J. usines a gaz* **45**, 220–1(1921).—The claim made in *C. A.* **15**, 2540, that Dr. Runkel was the discoverer of the process is denied; references are made to disprove it. Some question is raised as to the economy of the process as compared with the use of solvents as in the Bregeat process (*C. A.* **14**, 1602). J. L. WILEY

Blast-furnace gases. A. HUTCHINSON AND F. BAINBRIDGE. *Engineering* **112**, 66–7(1921).—The development of the use of blast-furnace gas and its cleaning is traced. The feature of new development is to concentrate by-product coke ovens, blast furnaces, steelworks and rolling mills in one plant, coupled with the utmost utilization of the surplus blast-furnace and coke-oven gases for power and heating purposes. Under such

conditions it should be possible to produce a ton of finished steel with the expenditure of not more than 1.6 ton of coal. Per ton of pig-iron, assuming a minimum surplus of 50% of blast-furnace gas together with the surplus coke-oven gas, 100,000 heat units should be available or an equivalent of 8–10 cwt. of coal. J. L. WILEY

Use of coke-oven gas. ANON. *Iron Coal Trades Rev.* **103,** 44(1921).—The Board of Trade has recently collected information concerning the production and disposal of coke-oven gas in relation to its bearing on coal conservation. In normal times as much coal is used in the production of blast-furnace coke as is carbonized for the manuf. of town gas. The requirements of domestic and industrial consumers in many districts are now being supplied from this source. Of the gas produced in by-product coke ovens, 50–60% is used for heating in the regenerative type and 66–100 % in the waste-heat type. This is possibly the most efficient means of using the gas, although it has been proposed to use blast-furnace gas for this purpose. The amt. of gas used by the coke-oven owners for purposes other than heating the ovens is 37,250 million cu. ft. annually, and a total of 7250 million cu. ft., including about 805 million cu. ft. run to waste, is available for disposal. Other and more economical methods of steam-raising than burning the gas under boilers will ultimately render available for other purposes a large part of the gas output not required for maintaining the carbonizing temps. The possibility of using the gas, compressed to 1000 lb. per sq. in., as a substitute for gasoline in internal-combustion engines is indicated, 250 cu. ft. of ordinary town gas being equiv. to 1 gal. of gasoline. J. L. WILEY

Introduction and development in the United States of the use of gas producers in the zinc industry. ANDRÉ SURNY. *Rev. metal.* **18,** 264–82(1921); 26 figs.—Three types of gas producers are described: those operated by hand, those mechanically operated, and those operated by both methods in combination. In class 1 are described the Hegeler, the Swindell, the Smith, the Westinghouse double zone, and the Duff and Bradley. This type gives general satisfaction where the fuel is of uniform and regular quality, compn. and size, and where skilled and careful workmen are employed. A cause of difficulty is the tendency to form air-holes and clinkers. In class 2 are the Taylor, the Chapman, the Hilger, the Morgan, the Hughes and the Wood. In this type the fuel bed is agitated to prevent air-holes and clinkers by revolution of 2 sections of the chamber, by mechanically operated pokers, or by a combination of both. Compared with class 1, this type of producer assures a gas of a more regular compn., a better utilization of the fuel, although with certain app. the loss of C in the ash is important, and a better condition of the combustion bed. The main disadvantage over the preceding type is that strict mechanical supervision must be maintained, as break-downs are frequent. The power required to operate them is about 1.5–2 h. p. per ton of fuel gasified per hr. The consumption of steam per kg. of fuel is considerable, about 0.4–0.6 kg., whereas with the former type it ranges from 0 to 0.3–0.4 kg. In class 3, 2 types are described: the Treat and the modified Chapman. In this class the charging and removal of ash are done by manual labor, the agitating of the bed mechanically. The cost of construction is, therefore, less than for class 2. J. L. WILEY

Fifty-seventh report of the Alkali Works Inspector. T. LEWIS BAILEY. *Gas J.* **155,** 151–2(1921); *Gas World* **75,** 74–6(1921).—The NH_3 products manufd. in the United Kingdom in 1920, calcd. in terms of 24.5% NH_3, were 418881 tons as compared with 397513 and 432551 tons in 1919 and 1918, resp. The production of dry neutral $(NH_4)_2SO_4$ is receiving increased attention, and many works are installing plants. An example of the application of superheated steam to sulfate stills is found at Dundee. A Sugden superheater is used fired with coke. The yield of sulfate has increased from 45 to 75 cwt. daily or 66% owing to the increased amt. of raw liquor able to be passed through the stills. The pressure of the dry steam is 22 lbs. and its temp. 355–400° F. Oxidation

of ammoniacal liquor by air. *Gas. J.* **155,** 161–2.—Tests were carried out in 1898 to det. if a preliminary treatment of the NH_3 liquor to effect oxidation of the sulfide to thiosulfate might not lessen the work thrown upon oxide purifiers attached to sulfate works. The results, however, were unfavorable, indicating that the rate of oxidation of $(NH_4)_2S$ to thiosulfate proceeds too slowly to render it practicable. Later in 1917 and 1918 attention was again directed to it by stoppages of the still by deposited S and particularly as to its effect in reducing the amt. of volatile cyanide in the liquors and indirectly in the crude coal gas entering the purifiers. It was thought that CN troubles might be relieved by admitting the air used to effect concurrent aeration of oxide in the purifiers at more than one point, in such a way as to oxidize $(NH_4)_2S$ with concurrent formation of thiocyanate without much exceeding the equiv. of polysulfide. The results however were fruitless. The manner of carrying out the tests is described. **Purification by oxide of iron.** *Ibid* 162–3, 214–16.—It is held that the physical condition of the oxide is the predominant factor in detg. its activity (Cf. Weyman, *C. A.* **14,** 1428, 2254, 2411). Scientific control of the gas-purifying process is essential; therefore, due coöperation must be had between the engineer and the chemist, inasmuch as purification should be carried out with as much care as the carbonizing process itself. The proper working for minimum handling of material involves: (1) selection of suitable material; (2) grid area not less than 0.5 sq. ft. per 1,000 cu. ft. of gas per 24 hrs. with efficient tar separator, and downward flow of gas through the purifier; (3) maintenance of a suitable reaction temp. in the boxes. *Burnt oxide and wood charcoal as catalysts.* Expts. with these materials have been carried out in the lab. only. The bulk of the burnt oxide used is Fe_2O_3; the total Fe content being over 65%. The results show that the material possesses all the properties of an active catalyst, promoting the combination of H_2S and O, and itself undergoing no apparent change of condition, either chemical or physical. It has one disadvantage, the fresh oxide is markedly more active as a catalyst than the product obtained after continued use. The few data obtained with wood charcoal establish the fact that its action is essentially different from that of oxide under the same conditions. With the burnt oxide, reactions are characterized by max. production of free S and minimum production of S oxidation compds.; with charcoal there is marked production of acid products with limited amts. of free S. A large initial absorption is noticeable with the fresh material, falling rapidly to a very low figure. Raising the temp. of the charcoal has little effect on the rate of absorption. Removal of the free S by CS_2, followed by aeration and drying at 70–80° has no beneficial effect. Also in *Chem. Age (London)* **5,** 122–3, 154–5(1921); *Chem. Trade J.* **69,** 91–3, 121–4, 157–8(1921). J. L. Wiley

Benzene recovery in medium and small gas plants. H. Menzel. *Gas und Wasserfach* **64,** 294–6(1921).—The Bamag type of benzene-recovery app. is particularly suitable for small gas plants. It is simple in type, inexpensive to construct and operate, washes the gas of naphthalene and benzene simultaneously with a considerable saving in wash-oil. The economic phases of gas-washing are discussed. J. L. Wiley

Distillation of tars in gasworks. H. De Savignac. Soc. Tech. du Gaz. *Gas World* **75,** 54(1921).—The process consists of blowing steam at 250° through tar heated to 200–250°. The volatile components go forward together, and with refrigerators in series there is progressive partial condensation and fractional sepn. The products are cooled by a counter-stream of tar. The first condensation tank receives anthracene oils and is steamed to prevent deposition of medium oils and naphthalene. The products then go to a tubular condenser and are collected, the remaining vapors then passing through a water-cooled tubular condenser, then through a worm in cold water. The condensation tanks now contain the heavy, medium and light oils. Tar containing as high as 14% of water can be handled by this method. By proper adjustments of

the flow of tar, the temp. of the receptacle, and the amt. of steam, pitch of any required degree of softness can be obtained, the proportion of heavy oils in the first condensation tank modified, and the line of demarcation between the light and medium oils varied. The process is easy to work, and the products are regular, uniform and pure. Also in *Gas J.* **155**, 545(1921). J. L. W.

Water-cooled ascension pipes. C. SCHURR. Soc. Tech. du Gaz. *Gas J.* **155**, 164–5(1921); *Gas World* **75**, 54(1921).—As the result of several trials, a water-cooled pipe has been designed, the use of which has eliminated all stoppages. The cause of stoppages is the distn. of the tarry deposits adhering to the walls of the pipe whenever the temp. is above 300°, leaving a deposit of pitch which continues to build up, thus reducing both the thermal conductivity and the free passage of the pipes. The removal of the cause depends on the one hand on cooling the pipes and on the other on reducing the temp. of the entering gas. At first a water spray at the base of the pipes was used which successfully prevented stoppages. But the holes in the spray, soon became choked and required frequent cleaning. Then water-jacketed ascension pipes were introduced similar in arrangement to that of surface condensers of modern electric plant. The water jackets are 2 m. high for the center retorts and 1 m. for the side retorts. The ascension pipes are 160 mm. internal diam. and are protected at the bottom from the high temp. and chemical action of the products deposited upon it by a cast-iron sleeve. The cooling water flows downwards, entering at 12° and leaving at 35–40°, and as it leaves at a pressure the lime deposits are negligible. The amt. of water used is about 60–72 cu. m. per furnace daily; one-third of it is afterwards used for coke-quenching. The temp. of the gas at the top of the ascension pipe never reaches 300° when that in the retort is 1140°, and the gas usually enters at 600° and leaves at 200°. The water jackets need to be cleaned of lime about once in 4 yr., and washed once in 2 yr. by passing weak HCl through them. No trouble is now experienced, the tars in the hydraulic mains are fluid, and the heats can be pushed as far as desired without fear of stoppages. J. L. WILEY

Determination of naphthalene in tar and tar oil. R. MEZGER. *Gas und Wasserfach* **64**, 413–16(1920).—M. reviews some of the methods found in the literature but discards them all in favor of Glaser's picric acid method and describes a slight modification of it. Instead of using air as the carrying medium of naphthalene, lighting gas, previously freed from CO_2, NH_3 and naphthalene, is passed through the app. at the rate of 25 l. per hr. The test lasts for 3½ hrs. The cork stoppers of the flasks are replaced by ground-glass stoppers. The whole of the picric acid soln., instead of only an aliquot portion, is used together with the washings of the filter. H_3PO_4 instead of H_2SO_4 is used to prevent any splitting off of SO_2, and to be sure that no acid vapors get into the picric acid the gas is washed with caustic potash between the Engler flask and the bulb tube. In order to obtain a uniform heating, a water bath is used instead of the air bath. By this modified method, all of the naphthalene can be converted into picrate and a more satisfactory detn. made than by the original method. J. L. WILEY

Sulfur compounds in coal tar. A. MAILHE. *J. usines gaz* **45**, 209–12(1921).—M. gives the properties of CH_3SH, C_2H_5SH, $(CH_3)_2S$ and $(C_2H_5)_2S$ found in coal tar, and also of thiophene and its derivs., and thionaphthene. J. L. WILEY

Repeated shut downs of coke ovens. J. M. HASTINGS, JR. *Iron Age* **108**, 73–4 (1921).—H. shows, by reference to the plant of Semet-Solvay ovens at Benwood, W. Va., which has been closed down several times since its construction in 1898, that, contrary to general opinion, a correctly designed and a properly constructed plant can be shut down completely without serious injury and without extraordinary labor or heavy repair expense on starting up. J. L WILEY

An aluminium coking apparatus with self-contained steam-superheater. HANS

SCHRADER. Mülheim-Ruhr. *Brennstoff Chem.* **2**, 182–3(1921).—The Al coking retort of Fischer and Schrader is often used in connection with a current of superheated steam, which removes the tar vapors from the zone of possible decompn. S. describes a modification of this app. in which satd. steam is introduced into a narrow hole bored in the thick Al walls of the retort; this hole passes in straight lines in through the supporting handle, vertically down one wall, twice across the bottom, vertically up another wall, into the cap through a coinciding hole, and down into the sample through a central tube. The steam is thus superheated to within 10–15° of the distn. temp. before coming in contact with the sample. W. B. V.

Determination of combustible gases in mine gases (WEIN) **7**. Purification of blast-furnace gas (GOUVY) **9**. Retort for distilling shale, oil-sand and coal (U. S. pat. 1,378,643) **22**. Ammonium sulfate (U. S. pat. 1,377,493) **18**.

FISCHER, FRANZ and SCHRADER, HANS: **Entstehung und chemische Strucktur der Kohle.** Essen: W. Girardet. 35 pp. M 5. For review see *Stahl und Eisen* **41**, 943(1921).

Artificial fuel. F. F. FOURNIER. Brit. 163,042, May 4, 1921. Crushed lignite is dried and exposed to the first stage of carbonization, mixed hot with H_2SO_4 or NaCl with or without pitch and the whole is finally compressed into blocks. Powdered lignite is conveyed to a drying and carbonizing stove and heated by hot air rising in temp. from about 30° to 125°. The elasticity of the cellulose tissues is thereby destroyed. After the addition of H_2SO_4 or NaCl with or without powdered pitch, the mixt. is kneaded and steam-heated until a homogeneous paste is obtained, which is fed into a high-pressure press to be formed into fuel of any desired shape. The % by wt. of the constituents may be: Lignite 85, acid 5, pitch 10; or without pitch, lignite 95, acid 5; or lignite 90, NaCl 1, pitch 9; or lignite 99, NaCl 1.

Liquid fuel mixture. C. LEPETIT. U. S. 1,377,992, May 10. A fuel adapted for use in internal-combustion engines is formed of EtOH 38.5–64, ether 34–57, $MeNH_2$, Me_2NH, or Me_3N 0.5–3 and ethyl or methyl formate 0.5–1.5 parts.

Gas producer. H. NIELSEN and F. D. MARSHALL. U. S. 1,378,369, May 17.

Gas producer. D. J. SMITH. U. S. 1,377,935, May 10. The producer has a fire bed shallow in proportion to its area and constantly agitated throughout with a supply of fuel in small regular quantities and an even high temp. is maintained in order to avoid slow distn. and produce clean gas in even quantity.

Gas generator. F. D. MOSES. U. S. 1,378,125, May 17. Connections are provided for introducing steam to the top or bottom of fuel in the generator.

Gas manufacture. H. NIELSON and J. R. GARROW. Brit. 162,459, Feb. 23, 1920. In a plant for the distn. of carbonaceous material by contact with hot producer gas, a number of producers are used to consume the whole of the coke obtained, and only one producer delivers gas to the retort so as to avoid undue diln. of the coal gas prior to the sepn. of tar oil. Detailed construction is specified.

Purifying gas. N. E. RAMBUSH. Brit. 162,553, May 21, 1920. In revivifying a sulfide sludge or suspension from gas-purifiers by subjecting the suspension to the action of a current of air, etc., the amt. of air allowed to escape from the app. is reduced as much as possible with the object of avoiding loss of S. The air may be circulated through a tower in a closed path by means of a pump, fresh air being supplied when required by means of valves. The suspension is circulated by a pump.

Separation of water from tar. BISMARCKHÜTTE. Brit. 163,011, May 6, 1921. H_2O is sepd. from coal tar by projecting the tar upwardly against a separating surface to which the H_2O adheres and from which it is collected. A suitable construction is specified.

Finely divided pitch. F. J. COMMIN. Brit. 162,727, Jan 2, 1920. Pitch in an extremely fine state of division is obtained by grinding, *e. g.*, in a ball mill, in the presence of a soln. of a peptizing agent such as alkali-casein, or resin soap. The liquid containing the pitch in a condition approaching the colloidal, is suitable for mixing with cellulose fiber for the prepn. of *cellulose fiber compns.*

Horizontal coke oven. O. PIETTE. U. S. 1,378,129, May 17.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

The extension of the term "mineral oil." FRITZ FRANK. Berlin. *Brennstoff Chem.* **2**, 188–9(1921).—Abstract of a paper presented before the Ver. deutsch. Chem., Stuttgart. In view of the confusion at present attaching to the term "mineral oil" F. proposes to define it as the entire class of aliphatic oils, basing his judgment on the history of the industry. In the discussion which followed, the proposal was vigorously attacked, and others were advanced, *e. g.*, "unsaponifiable oils" (Graefe), "oils which cannot be esterified" (Schneider). The Division of Fuel- and Mineral-Oil Chemistry will shortly publish an "official" definition of the term. Also in *Z. angew. Chem.* **34**, Aufsatzteil, 497–8(1921). W. B. V.

Possibilities of producing oil from oil shale. MARTIN J. GAVIN. Bur. of Mines, *Repts. of Investigations* **2176**, 7 pp.(1920).—Among the most promising substitutes for petroleum is shale oil. In Australia, France and Scotland, shale oil has been manufd. commercially but only in Scotland is the industry of any importance today. A brief description of the manuf. of shale oil in Scotland is given with statistics of yields of oil, NH_3, coke, etc., and methods of refining. Much of the American oil shale will yield more oil than the av. Scotch shale. So far what little oil has been made experimentally in this country has been inferior, from the refiners viewpoint, to that made in Scotland, but the yields of NH_3 compare favorably with those from Scotch shales. Based on Scotch practice, which very probably is not well adapted to our shales, to establish an industry in Colorado which would produce 50,000 bbls. of oil a day would require for the retort plant over $160,000,000, and $50,000,000 capital for building the necessary refineries. The U. S. industry is in the exptl. stage and much research and development are necessary. H. S. BAILEY

Liquid fuel for steam raising. N. A. ANFILOGOFF. *J. Soc. Chem. Ind.* **40**, 205–9R (1921).—Fuel oil is more efficient than coal for boilers because it gives a flame which is more concd., more easily controlled, and more economical. Theoretically, one lb. of oil has about the same evapg. value as 1.5 lb. of coal; in practice 1 lb. of oil will do the work of 1.95 lb. of coal. To get the most efficient results from liquid fuel 2 essentials must be provided: (1) means to convert the oil into a heavy vapor; (2) sufficient air to support combustion. The oil is burned not as a true vapor but as a heavy mist. Two types of burners are in use: (1) those in which the oil under pressure is atomized through a small aperture; (2) those in which the oil is atomized by a stream of air or steam. For efficient combustion the air supply must be carefully regulated. The proper quantity of air in cu. ft. may be roughly estimated by dividing the calorific value of the fuel in B. t. u. by 100. Details are given of the changes necessary to convert a Lancashire or a Babcock and Wilcox water-tube boiler from coal to oil A good fuel oil should (1) have a flash point (closed test) not less than 150° F., (2) be sufficiently fluid to be pumped at all temps., (3) not contain more than 1% of moisture, (4) be free from particles of C or other solid matter. T. S. CARSWELL

Commercial benzines. A. GANSWINDT. *Neueste Erfin. u. Erfahr.* **37**, 74–9(1920); *Chimie & industrie* **5**, 416(1921).—Brief review of the different grades of benzine,

their origin, and methods of prepn., including the catalytic reaction of H on CO or on CO_2 in the presence of Co oxide or of osmic acid. A. P.-C.

Removal of the fluorescence of vaseline oils. G. MEYERHEIM. *Deut. Parfümerie Ztg.* **6**, 123–5(1920); *Chimie & industrie* **5**, 416(1921).—Mineral oils intermediate between kerosene and lubricating oils are used in perfumery, after removal of their fluorescence and odor. The latter is removed by repeated steam distn., rejecting the head fraction each time. The fluorescence (blue for Russian and greenish for Pa. oils) is due to hydrocarbons such as pyrene and chrysene. It may be eliminated: (1) by treating with H_2SO_4, removing the sulfonic acids with alkali, distg. with steam, and rectifying; (2) by adding yellow compds. such as nitrated or brominated and nitrated naphthalenes, or quiholine yellow; (3) by treatment with O in the presence of ultra-violet light. Methods of identifying the oils are described. A. P.-C.

Wood distillation in the Argentine Republic. MARTINIANO L. PONDEL AND JUAN PELISCH. *Anales soc. quim. Argentina* **8**, 242–67(1920).—A survey of this industry as developed in Argentina. Refined acetic acid and methanol are made on a large scale in a number of plants but little or no acetone. Many types of retorts are used.

L. E. GILSON

Action of certain rock formations on petroleum (LONGOBARDI) **8**. Petroleum genesis and geology (HUNT) **8**. 44th Annual Report H. M. Inspectors of Explosives (COOPER-KEY, *et al.*) **24**.

De l'emploi des combustibles liquides. Paris: Librairie Desforges 29 quai des Grands-Augustens. 5 f. For review see *Rev. l'ing. index tech.* **27**, 477(1921).

DUMERNY, P. and NOYER, J.: **Wood Products.** London: Messrs. Scott, Greenwood & Son. 21s net. For review see *Paper Makers' Monthly J.* **59**, 295(1921).

MARCUSSON, J.: **Die Natürlichen und Künstlichen Asphalte.** Leipzig: Wilhelm Engelmann. M 26. For review see *Kunststoffe* **11**, 101(1921).

Distilling petroleum. E. O. HICKS. U. S. 1,378,229, May 17. In treating petroleum oils b. above 260° to obtain products of low b. p., the material is heated to 340–450° and the vapors are condensed. The condensate is revaporized from condensate receptacles within the still and the revaporized material is condensed. The distn. is conducted under 4–5 atm. pressure and gas formed is released from the app. as required.

Distilling oils. J. G. P. EVANS. Brit. 162,873, March 9, 1920. In refining crude oil, the upper layers of oil in a conical still are heated by an elec. heater or by other means and the vapors evolved are condensed in the space between the still and an outer insulated jacket. The condensate is collected by a series of channels having drip flanges above them, so as to obtain fractions of different b. p. The crude oil is continuously supplied by a pipe at the base of the still, and the residuum is withdrawn by a pipe having a small opening at the top to prevent siphoning. A temp. of 560° F. may be maintained at the top of the still, and the oil being supplied at an ordinary temp. of 60° F., a temp. of about 310° F. is obtained at the line which passes through the center of gravity of the still.

Retort adapted for distilling shale, oil-sand or coal. A. V. YOUNG. U. S. 1,378,643, May 17. The retort is inclined and has an upwardly arched bottom over which a conveyer runs.

Cracking petroleum oils. A. ROGERS. U. S. 1,378,424, May 17. In cracking oil to form motor fuel, the oil is mixed with about the amt. of steam to vaporize it at a temp. of 315° and produce a vapor mixt. substantially free from liquid and the mixt. of oil vapor and steam is progressively heated to about 425° in pipes heated internally and externally by furnace gases.

Still for cracking and refining petroleum products. W. H. YOUNG. U. S. 1,378-307, May 17. Petroleum and steam are passed through heated pipe coils within a furnace.

Destructive distillation in situ. D. DIVER. Brit. 162,337, Dec. 23, 1919. In the recovery of oils from bitumen and shale by destructive distn. *in situ*, the heat is supplied from a source located within the strata undergoing treatment. A suitable construction is specified.

Electric heating apparatus for regulating the temperature in oil stills. A. F. G. C. P. J. VON GROELING. U. S. 1,378,066, May 17.

Apparatus for melting and handling asphalt. M. P. WALL. U. S. 1,378,637, May 17.

23—CELLULOSE AND PAPER

A. D. LITTLE

The Elmendorf paper tester. ANON. *Elec. Rev.* (Chicago) **79**, 180(1921); 2 illus. —This instrument was developed by the U. S. Forest Products Lab. The tester measures with accuracy and very quickly the tearing strength of all grades of paper, including insulating papers. It is a common practice to judge the strength of paper by tearing it with the hands. The E. tester does the same thing mechanically. A strip of paper of standard dimensions is clamped fast and a knife handle is depressed, cutting a split in the specimen which dets. an exact length to be torn. A friction pointer is set against a fixed stop and the spring stop is released; the paper tears and its tearing strength (or resistance to tear) is indicated by a pointer attached to a weighted arm. Full details are given. C. G. F.

The testing of cardboard: elasticity or rigidity, and folding. RAYMOND ISNARD. *Papeterie* **43**, 578–86(1921); cf. *C. A.* **15**, 1214.—The general principles of testing the strength of beams can be applied to the testing of the rigidity, or, what comes to the same thing, the elasticity, of cardboard; if a strip of cardboard be placed on 2 supports at a distance l apart and subjected to a load P at its center, the deflection f is $Pl^3/48.EI$ where E is the modulus of elasticity and I the moment of inertia of the section. In the app. described a strip of cardboard 1 × 10 cm. is supported on knife-edges exactly 50 mm. apart, so that 25 mm. project at either end. A graduated lever, pivoted at one end, carries a third knife-edge by means of which the load is applied to the middle of the test strip. The wt. of the lever and knife-edge is balanced by means of an adjustable counterpoise, and the load is varied by means of a rider (or riders) on the lever arm. The deflection on applying the load is read by means of a mirror fixed to the lever and a scale graduated in mm. Then if d and D be the resp. distances of the deflecting knife-edge and of the scale from the mirror, P the equiv. load at the center at the test strip, n the reading on the scale, and e the thickness of the cardboard, $E = \frac{6250P}{ne^3d} \cdot \frac{D}{d}$. As the possible error in the detn. of the thickness is about 2%, and E involves e^3, the limit of accuracy is no greater than about 6%. After taking the reading, if the test strip be folded completely over (presumably without creasing), weighted in this position for 15 min., released and allowed to stand for several hrs., it will be noted that it finally attains a definite "fold angle," which varies from 20–5° for very rigid boards, to 60° for roofing felts. Comparative results on different samples can only be obtained by applying the test under exactly the same conditions. If properly carried out, this test will class boards in the same order as the detn. of elasticity. An examn. of the fold can furnish valuable information as to the compn. and quality of the cardboard. A. P.-C.

The use of "rifatto" in the manufacture of cellulose for paper. STEFANO DI PALMA. *Staz. sper. agrar. ital.* **53,** 393–4(1920).—"Rifatto" is the woody residue remaining after the extn. of the juice from the roots of *Glycyrrhiza glabra* Lin. On treatment with dil. HCl and washing with H_2O fine brownish fibers remain which are decolorized by the action of chloride of lime or the hypochlorites. Air-dried they have an ash content of 6%, mostly carbonates, chlorides, sulfates and phosphates of Ca, Na and K, with Si and Fe. Containing about 50% crude cellulose it is well adapted for the prepn. of paper pulp. ALBERT R. MERZ

Utilization of residual liquors in the manufacture of wood pulp. H. BRAIDY. *Rev. gén. mat. color.* **25,** 65–70, 85–90(1921).—The object of this study was to exam. the feasibility of producing EtOH from the waste liquors of the sulfite process of pulp manuf. The general compn. of the liquors, the procedures recommended for their utilization, and the economic outlook offered by the operating of these procedures are discussed. On each of the various points there is an assemblage of information quoted from the literature. L. W. RIGGS

The Crown Williamette paper plant. W. A. SCOTT. *Elec. Rev.* (Chicago) **79,** 189–91(1921).—A brief account of the large pulp and paper mills and processes, emphasizing the elec. features. C. G. F.

Sulfite liquor. ROBERT SCHWARZ AND HELLMUTH MÜLLER-CLEMM. *Z. angew. Chem.* **34,** Aufsatzteil, 272–5(1921).—In order to det. the relations in the formation of sulfite liquor, the equil. between SO_2 and $Ca(HSO_3)_2$ in a system contg. $Ca(SO_3)_2$ has been detd. at various temps. and concns. of free SO_2. It is shown that, in this system, at each temp. and independent of the concn. of the original soln., the quotient of the bound and free acid is const. and approx. 2. The amt. of the bound bisulfite and the free SO_2 increases with decreasing temp. In this there is an anomaly, however, in that between the temps. 30° and 22°, variations occur which lead to a disproportionately large increase of the total content, reaching a max. at 26°. The max. soly. of the $Ca(SO_3)_2$ occurs at this temp., which corresponds to the practical observation that the highest content of bound SO_2 is obtained when the tower liquor is kept at 26–28°. Up to an original content of SO_2 of 6.5%, the quotient of the bound by free acid is independent of the initial concn. The exptl. detn. of this relation at still higher temps. is accompanied by difficulties. If one satd. a soln. in equil. with SO_2 at any given temp., one finds an increase in bound as well as free acid. The behavior of the 2 components with decreasing temp. is in favor of the free acid. C. J. WEST

Nitrocellulose and its solutions as applied to the manufacture of artificial leather (TUCKER) **29.** Finely divided pitch (for cellulose fiber compositions) (Brit. pat. 162,727) **21.** Dyeing cellulose acetates (U. S. 1,378,443) **25.**

Indian Trade Enquiry Reports on Timbers and Paper Materials. London: John Murray, Albemarle St. W. 4s net. For review see *Paper Maker's Monthly J.* **59,** 295(1921).

Papier-Kalender 1921. Jahresbericht über wichtige Neuerungen in der Papierfabrikation und technisches Hilfsbuch nebst Adressbuch. Begründet Wilhelm Pfaff. Bearbeitet Willy Ebert. 35 Jahrgang. Dresden- A.: Johannes Henkler, Pirnaische Strasse 161. M 12.75. For review see *Wochbl. Papierfabr.* **52,** 418(1921).

Calcium bisulfite. G. A. RICHTER. U. S. 1,378,616, May 17. $Ca(HSO_3)_2$ liquor for cooking wood pulp is formed by acidulating H_2O with SO_2 in an absorbing chamber and then reacting upon lime with this soln. in another absorbing chamber.

Calcium bisulfite liquor. G. A. RICHTER. U. S. 1,378,617, May 17. A $Ca(HSO_3)_2$

pulp cooking liquor is prepd. by reaction of H_2O and SO_2 upon pulverized magnesian limestone.

Cellulose ethers. L. LILIENFELD. Brit. 163,016, May 12, 1920. In the production of ethers of cellulose and its conversion products, etc., the cellulose is simply impregnated with caustic alkali soln. and then treated with the alkylating, aralkylating, or arylating agents without removal of the excess of caustic alkali soln. and without being subjected to the more or less prolonged ripening process necessary to the production of alkali-cellulose.

Cellulose and other carbohydrate ethers. L. LILIENFELD. Brit. 163,017, May 12, 1920. In the production of ethers of cellulose, starch, dextrin, etc., their conversion products and derivs., the cellulose, etc., is treated in the presence of at least 15 parts of a 30–50% caustic alkali soln. with alkylating, aralkylating or arylating agents.

Cellulose and other carbohydrate ethers. L. LILIENFELD. Brit. 163,018, May 13, 1920. In the production of ethers of cellulose, starch, dextrin, etc., their conversion products and derivs., the cellulose, etc. before reaction with the alkylating, aralkylating, or arylating agents, is treated with solid caustic alkali either in the dry state or in the presence of so little H_2O or caustic alkali soln. that at least a part of the caustic alkali remains undissolved; the products—films, celluloid, artificial filaments, and insulating-materials—prepd. from the ethers eventually obtained, are distinguished by their water-resisting properties. The incorporation of the cellulose, etc., with the caustic alkali may be conducted in the presence of air or inert gas, or *in vacuo*, and at ordinary temps., or with heating or cooling; and the treated cellulose may before etherification be freed wholly or partly from the H_2O contained therein, and may be immediately treated with the alkylating, etc., agent, or after standing. The etherification may be conducted so as first to form a lower ether, which may be converted into a higher ether by treatment with further quantities of caustic alkali and alkylating, etc., agent.

Viscose filaments and films. E. BOUILLON and M. WORMS. Brit. 162,759, Jan. 31, 1920. A pptg. bath for use in the manuf. of filaments and films from viscose contains $Al_2(SO_4)_3$, Na_2SO_4, and an inorg. acid such as H_2SO_4, or, alternatively, in place of the acid, $Na_2S_2O_3$ or $NaHSO_3$.

Spinning nitrocellulose solutions. A. DRYEN. U. S. 1,377,761, May 10. A coagulating bath of 30–75% H_2SO_4 soln. in H_2O is used at the issue orifice in forming threads, filaments, artificial straw or films from nitrocellulose solns.

24—EXPLOSIVES AND EXPLOSIONS

C. E. MUNROE

Liquid explosives. S. NAUCKHOFF. *Tekn. Tids., Kem. Berg.* **51**, 52–9(1921).—Value, cost, transportation and charging of liquid explosives are discussed. Attention is paid primarily to petroleum-soaked material dipped in liquid air. A. R. Rose

Some war developments of explosives. ROBERT ROBERTSON. *Nature* **107**, 524–7(1921).—The high explosive shell adopted is illustrated and described in its various parts, together with the cordite by which it was propelled, the $Hg(ONC)_2$, tetryl, and intermediate explosives in the initiating system, and the bursting charge. Because of the magnitude of the acceleration imparted to all parts of the shell when fired from the gun, a column of sensitive explosive exceeding a certain length and weight will be liable to detonate; therefore the length of the column must be graduated in proportion to sensitiveness and the quant. detn. of this characteristic is of marked importance. The values of *insensitiveness* found were $Hg(ONC)_2$ 10, nitroglycerin 13, dry gun cotton 23, tetryl 70, TNA 86, picric acid 100, TNT 115, and amatol, 80/20, 150. The *violence* was measured by the pressure bar method. The *heat of detonation* in cals. per g. (water

gaseous) and *total gas per g.* found were picric acid 914 cals. 744 cc., TNT 924 cals. 728 cc., amatol 40/60, 920 cals. 892 cc., amatol 80/20, 1004 cals. 907 cc., tetryl 1090 cals. 794 cc., gun cotton 892 cals. 875 cc., nitroglycerin 1478 cals. 713 cc. The *rates of detonation* in m. per sec. under a given *density of loading* were nitroglycerin 8000 m. d. liquid, tetryl 7520 m. d. 1.63, gun cotton (dry) 7300 m. d. 1.20, picric acid 7250 m. d. 1.63, TNT 6950 m. d. 1.57, amatol, 40/60, 6470 m..d. 1.55, amatol, 80/20, 5080 m. d. 150. A table is given showing the *pressures developed by NH_4NO_3, TNT and mixts.* of these in various proportions (*amatols*), in tons per sq. in. in 0.5×10^{-5} secs. The pressure found for NH_4NO_3 was 12.5 tons, with 0.5% TNT 15.2 tons, and the pressure steadily rose with increased % TNT until for TNT only (d. 1.55) it was 55 tons. The 40/60 amatol varies little from TNT. The 80/20 has a decidedly lower pressure and rate of detonation but fragments the shell satisfactorily and the slower development of the pressure together with its high calorific value may be of advantage in enabling the fragments to acquire a higher velocity. The *explosives manufacture* attained a *weekly output* of 1500 tons TNT, 300 tons picric acid, 3000 tons NH_4NO_3 and 2000 tons of cordite. For this there were used weekly 6600 tons pyrites, or 2700 tons of S., 8300 tons $NaNO_3$. 700 tons of C_7H_8 (from 600,000 tons of coal), 162 tons of synthetic C_3H_5OH (equivalent of 1,000,000 tons of coal), 700 tons NH_3 (from 250,000 tons of coal), 374 tons of glycerol (from 2700 tons of fat), 700 tons of cotton (from 1060 tons of waste), and 1200 tons of alc. and Et_2O (from 4200 tons of grain.). England was dependent on overseas transport for pyrites, S Chili nitrate and cotton. CHARLES E. MUNROE

44th annual report. H. M Inspectors of Explosives. A. COOPER-KEY, *et al.* H. M. Stationery Office, London. 1921. 29 pgs.—This rept. on the operations for 1920, while giving the data and covering all the points required by the Explosives Act of 1875, is limited to the bare essentials and is published in a form that will surprize those familiar with the previous repts. Expts. were limited to some tests of *liquid-air explosives in stump blasting*, the results of which appeared satisfactory, and, at the Rotherham Testing Station, in *substituting natural gas for coal gas*. The repts. on accidents include that of a motor truck laden with 500 gals. of petrol in tins whose rear axle broke going down hill. By the fall some of the cans were so damaged that petrol escaped and became ignited by sparks from the brakes. Also that at a petroleum depot where 12,000 gals. were stored underground and 1000 gals. in 2-gal. cans stored in a corrugated iron shed just adjoining. Fire broke out and consumed the above-ground material without affecting the underground tank. Further, on Sept. 20th, 1919, at Calcutta, a ton of CaC_2, in damaged drums, was being emptied into a dock when the generated C_2H_2 became ignited by some means and a terrific explosion ensued, causing the death of 4–5 persons. CHARLES E. MUNROE

The explosives industry in Canada in 1918. R. H. COATS. *Dominion Bur. of Statistics* Canada 1921. Mimeographed. 7 pp.—This is an advance chapter of "Chemicals and allied products in Canada in 1918." During 1918, the last year of the war, 5 firms manufd. *explosives* in Ontario, 3 in Brit. Columbia and 3 in Quebec, the total investment being $19,172,539, cost of materials used $23,125,839, and value of products $41,477,828 while 4708 wage earners and 251 salaried employees were engaged in the work. In addition there were 3 establishments making *matches* and 2 making *fireworks* with a total investment of $2,364,289, cost of materials $788,182 and value of products $1,604,342, there being 570 wage earners and 47 salaried employees engaged in the work. The chief explosives, as to quantity and value, produced in 1918 were the military ones, yet in that war year there were made 21,674,046 lbs. of dynamite and 796,225 of blasting powder. The materials used are enumerated in greater detail than has been permitted in U. S. census reports in the past. The statement is made that with the passage of the Explosives Act a coöperative scheme for taking these statis-

tics has been evolved and that the next report "will be much more detailed than it has been found possible to make this." CHARLES E. MUNROE

A characteristic reaction for the detection of mercury fulminate. A. LANGHANS. *Z. anal. Chem.* **60**, 93–4(1921); cf. *C. A.* **14**, 1041.—Moisten the fulminate (20 pts.) with alc. (5 pts.), and water (50 pts.); add while shaking 100 pts. of a 20% soln. of Schlippe's salt. An egg-yellow ppt. is formed which in 5 min. turns green and on long standing becomes black. If the soln. is filtered, white, lustrous crystals gradually form in the filtrate and HNO_3 gives a beautiful red coloration. The red dyestuff is sol. in ether. The reaction is sensitive but cannot be studied farther at this time because expts. with explosives are no longer permitted in the conquered cities of Germany.

W. T. HALL

Report of Explosives Division Department of Mines (Canada) for 1920. G. OGILVIE, 19 pgs.(1921).—This report deals with new legislation and the operations under the Act proclaimed Mar. 1, 1920. Under "Accidents in manufacture," the explosion of 7700 lbs. of nitroglycerin in 4 tanks is reported and it is noted that although several substantial pieces of débris were projected up to distances of 250–300 yards the great mass of it lay within 60 yards of the site on which a crater 40 ft. in diam. and 15 ft. deep was formed. Also that in the burning of a building in which TNT was being screened 3000 lbs. of TNT was destroyed without explosion "as was to be expected." In a pulverizing house fire arose through the spontaneous ignition of charcoal and S on the mixt. being emptied from a barrel. In the appendices the production and importation of explosives into Canada, the accidents occurring in 1919 and 1920 and a provisional list of "Authorized explosives" is given. CHARLES E. MUNROE

The Aetna Company. ANON. *Hercules Mixer* **3**, 153–6(1921).—Apropos of its consolidation with the Hercules Powder Co. a review of the history and war activities of the Aetna Explosives Co. is given. The article is of special interest to technical chemists because of the numerous excellent illustrations showing the construction and operation of a dynamite plant. CHARLES E. MUNROE

An unusual hazard in reopening long-flooded timbered metal mines. D. HARRINGton. Bur. of Mines, *Repts. of Investigations* Ser. No. **2255**, June 1921. Mineographed. 3 pgs.—Several explosions occurring in reopened metal mines have been found due to marsh gas formed by reaction with timbers submerged in water. The precautions to be taken are indicated. CHARLES E. MUNROE

Gases produced in the use of carbon tetrachloride and foamite fire extinguishers in mines. A. C. FIELDNER AND S. H. KATZ. Bur. of Mines, *Repts. of Investigations* No. **2262**, 5 pp.(1921).—Tests on CCl_4 extinguishers and "foamite fire-foam" extinguishers show that the former produces poisonous gases (cf. *C. A.* **15**, 294), while after use of the latter, the compn. of the atmosphere is about the same as that surrounding any wood fire. "Foamite fire-foam" extinguishers contain $Al_2(SO_4)_3$ soln. in a central cylindrical chamber and Na_2CO_3-licorice soln. in the annular space around it. The central tube is closed with a stopper, which falls out when the extinguisher is inverted. CO_2 is generated and quickly produces sufficient pressure to eject a foamy liquid a distance of 30–40 ft. from the nozzle. Full details of the tests and results of the analyses are given. Foamite produces no dangerous gases. CCl_4 extinguishers are suitable for elec. mine locomotives because CCl_4 is a nonconductor and entries and haulage ways are usually well ventilated. W. H. BOYNTON

Determination of combustible gases in mine gases (WEIN) **7**. Trinitroresorcinol (Brit. pat. 162,578) **10**.

PSENICA, N: **Die nitrierte Nesselfaser vom technologischen und sprengstoff-**

technischen Standpunkte. Leipzig and Vienna: Franz Deuticke. M. 20. For review see *Z. ges. Schiess Sprengstoffw.* **16**, 102(1921).

Pyrotechnic compositions. A. BROCK and R. M. BUTT. Brit. 162,697, Nov. 3, 1919. Pyrotechnic compns., percussion caps, and fuses are consolidated by means of a sol. silicate such as Na or K silicate instead of the usual starch, gum, dextrin, or sugar.

Colored smoke. E. C. WEISGERBER. U. S. 1,377,533, May 10. A compn. producing red colored smoke and adapted for use in military operations is formed of $KClO_3$ 30, lactose 18, I 30 and *p*-nitroaniline 54 parts.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Note on the development of the indigo industry in Assam in conjunction with tea and other crops. W. A. DAVIS. *Agr. Research Inst., Pusa, Indigo Pub.* No. **8**, 17 pp.(1921).—The time required for steeping varies with the bacterial content of the water used; the following method of control is proposed: 6 to 8 drops of dil. NH_4OH are added to 5 cc. of the liquor from the bottom of the vat, which is then dild. to 250 cc., shaken 5 min. and allowed to stand 10 min. Its color is observed in a Nessler cylinder. Samples are taken at half-hour intervals until a max. color is reached. Over-steeping causes the color to fade again. Indigo seet (refuse from the vat) is used as a fertilizer for tea, etc. H. W. EASTERWOOD

The loss of indigo caused by bad settling and the means of obviating this. W. A. DAVIS. *Agr. Research Inst., Pusa, Indigo Pub.* No. **3**, 16 pp.(1918).—The use of Dhak gum in indigo settling vats often increases the yield from 35% to 70%. H. W. E.

The future prospects of the natural indigo industry. W. A. DAVIS. *Agr. Research Inst., Pusa, Indigo Pub.* No. **4**, 19 pp.(1918); cf. *C. A.* **15**, 2686.—The future of the natural indigo industry depends on the systematic application of phosphatic fertilizers. H. W. EASTERWOOD

The conditions affecting the quality of the Java indigo plant (leaf yield and richness of the leaf in indigotin). W. A. DAVIS. *Agr. Research Inst., Pusa, Indigo Pub.* No. **7**, 33 pp.(1920).—Soils low in N and high in humus and available P_2O_5 give the highest indigotin content in the leaf. Cover crops of wheat, mustard, etc., increase the quality of the indigo by removing a part of the available N from the soil. H. W. EASTERWOOD

An improved method of preparing indican from indigo-yielding plants. BHAILAL M. AMIN. *Agr. Research Inst., Pusa, Indigo Pub.* No. **5**, 9 pp.(1919).—This is an improvement on the Perkin and Bloxam method. The yield is increased by 40%. The fresh leaf is extd. with boiling H_2O and the impurities are pptd. with lime. The excess lime is removed with CO_2. The filtrate is concd. and the indican extd. with acetone. The ext. is evapd. on the water bath to remove the acetone and the indican crystd. from a small amt. of H_2O by cooling with ice. The crude crystals are purified by soln. in 96% alc. and pptn. with dry benzene, yielding anhydrous indican, m. 176–78°. H. W. EASTERWOOD

Industrial poisoning in making coal-tar dyes and dye intermediates. ALICE HAMILTON. U. S. Dept. Labor, Bur. Labor Statistics, *Bull.* No. **280**, 87 pp.(1921).—This report is based on 36 inspections of American factories producing crudes, intermediates and colors, made during the years 1916–19, and visits to 5 English, 1 France and 2 German establishments during 1919. The various toxic coal-tar products are described with details of manuf., of conditions under which workmen are liable to suffer

from poisoning, and of the symptoms and treatment in case of each product. Aliphatic and inorg. compds. used in the processes are also considered as to their harmful qualities. The processes of sulfonation, caustic fusion, nitration, reduction, chlorination, alkylation, oxidation, carboxylation, liming, condensation, diazotization and coupling as practiced in factories are described with reference to such features of the processes as are liable to injure the workmen. The making of intermediates is on the whole attended with more risk of poisoning than the making of finished colors; also the benzene, toluene and xylene intermediates are much more dangerous than naphthalene and anthracene intermediates. The prevention of poisoning depends upon the coördination of many factors, among which are cleanliness of all parts of the buildings, dry floors, all fumes, dust and steam removed at their sources, strict medical supervision, proper food, clothing and baths, and most important, workmen of sufficient intelligence and tractability to cooperate in the measures for making their work healthful. At present in American practice some of these factors are emphasized and others ignored. L. W. RIGGS

Tests for fastness of dyes are devized for use of textile trade by German commission. ANON. *Textile Colorist* **43**, 537–41(1921).—The standardized recommendations of the Echtheitskommission for testing the fastness of dyed cotton and wool. The following fastness tests and norms for same are given: *I* Washing and boiling colored cottons; *II* washing of colored wools; *III* rinsing in cold water for cotton and wool; *V* ironing of cotton and wool; *VI* SO_2 on cotton and wool; *VII* perspiration for cotton; *VIII* perspiration for wool; *IX* (alkaline) dust on cotton and wool; *X* boiling acid on cotton; *XI* acid on wool; *XII* acid on cotton; *XIII* Cl on cotton; *XIV* mercerizing on cotton; *XV* bleaching on wool; *XVI* fulling on wool; *XVII* carbonizing (H_2SO_4) on wool; *XVIII* decating on wool; *XIX* salt water on wool; *XX* light on cotton and wool.

CHAS. E. MULLIN

A study of the variations in hematin dyeings with different methods of chrome mordanting. CARL W. STAPLES. *Textile Colorist* **43**, 463–6, 528–31(1921).—Both shade variation and intensity of exptl. dyeings by 9 different methods of mordanting and 3 methods of dyeing with 2 strengths of dyestuff, were studied by means of the Hess-Ives tint photometer. Methods of mordanting were as follows: (*1*) Boil 1.5 hrs. in 2% dichromate and 2% oxalic acid. (*2*) Boil 1.5 hrs. in 2% dichromate and 1.5% K H tartrate. (*3*) Boil 15 min. in 2% dichromate; then add 7% H_2SO_4 and boil 0.5 hr. more. Dry and expose to Hg-vapor light for several hrs. until reduced. (*4*) Boil 1.5 hrs. in 2% dichromate and 5% lactic acid. (*5*) Warm to 75–80° in 6% AcOH. After 0.5 hr. add 1% chromic acid and work 0.5 hr. Add 6% $NaHSO_3$, reheat to 75–80° and work for 0.5 hr. Dye with addition of 1% NH_4OH. (*6*) Same as 4 but formic acid substituted for lactic. (*7*) Use 1% dichromate instead of 2%, H_2SO_4 and K H tartrate. (*8*) Boil 15 min. with 2% dichromate, add 3.3% H_2SO_4 and boil 0.5 hr., squeeze, enter in bath of 6.6% $NaHSO_3$ and 3.3% H_2SO_4, and work 0.5 hr. (*9*) Chrome alum equivalent to 2% dichromate with 12 equivalents of K H tartrate. The dyeings with both 1% and 5% hematin were made as follows: (*a*) Enter in 95° dyebath and work until bath exhausts; then add 1% dichromate and work 0.5 hr. more. (*b*) Same as *a* but the dichromate treatment is omitted. (*c*) Work 1.25 hr. in boiling bath, then 15 min. in cooling bath with addition of AcOH to exhaust. On stock mordanted with chromic acid, no AcOH was used. Ten tables are given, showing tint-photometer readings for relative strength of dyeings; effect of temp. differences and oxidizing agent; variations in % of red, green, and blue-violet; and also the strength, and stretch of the dyed fiber.

CHAS. E. MULLIN

Flower colors—their use in dyeing and dye-research. A. J. HALL. *Textile Colorist* **43**, 517–9(1921).—A brief review of the work upon the flower coloring materials and its possible application.

CHAS. E. MULLIN

Notes on the preparation of methylene blue printing pastes and their fixation. RAFFAELE SANSONE. *Textile Colorist* **43**, 519–20(1921).—Five formulas are given. CHAS. E. MULLIN

Tartar—its uses and advantages. JOSEPH E. TRAVERS. *Textile Colorist* **43**, 531–2(1921).—A brief discussion of the advantages of tartar in mordanting H_2SO_4 and Al_2Cl_6 carbonized stock, high grade clothes and shoddy, as well as in top- and metachrome dyeing. CHAS. E. MULLIN

Steam consumption tests. V. WICHUM. *Textile Colorist* **43**, 461–2, 535–6(1921).—Figures are given from 27 actual tests made of the steam consumption in boiling a standard Rodney Hunt piece dye machine, controlled by a hand valve and by the Tagliabue Roesch automatic time-temp. controller. A decided saving in steam is shown by the automatic controller. CHAS. E. MULLIN

The use of sodium and potassium salts in dyeing and printing fabrics. O. PIEQUET. *Chimie & industrie* **5**, 208–9(1921).—Discussion of the relative merits of the chlorates, dichromates, and ferrocyanides of Na and K in the dyeing and printing of fabrics. A. P.-C.

Mordants and their dyeing by the electrolytic process. FELIX DRIESSEN. *Bull. soc. ind. Mulhouse* **87**, 140–52(1921).—A report of this paper is given by Battegay Perrin and Ch. Sunder. While admitting the interesting facts contained in the paper, they state that the theoretic conceptions of the author in relation to electrical phenomena on the one hand, and the phenomena accompanying mordanting on the other are of the nature to provoke controversy. Opinions are reserved as to the practical nature of Driessen's suggestions. . . L. W. RIGGS

Report on Sealed Notes Nos. 2087 and 2119 by H. Sunder: Alizarin red vapor on fibers free from oil. Alizarin rose with mixture of sulforicinate and sulfoleate of tin. LOUIS DISERENS. *Bull soc. ind. Mulhouse* **87**, 137–9(1921).—The particular point of Sunder's recipe was the use of tin lactate in place of the oxalate. Tin lactate had been employed in similar dyes for a number of years before the date of Sunder's note. L. W. RIGGS

Black dyeing of cotton yarn. JULIUS SCHMIDT. *Deut. Färber-Ztg.* **57**, 605–6 (1921).—Formulas and directions are given for dyeing cotton yarn with substantive or benzidine dyes, diazotizing or developing dyes, sulfur dyes in an alk. Na_2S bath without mordant, and oxidation dyes such as aniline black. L. W. RIGGS

The pinking of bleached cottons. WILLIAM B. NANSON. *Textile Am.* **36**, No. 2, 16–7(1921).—The color may be caused by aniline vapor or its homologs, in the presence of either Fe or oxycellulose. The pink formulae and *Bacillus prodigiosus* also cause pinking under certain conditions. Slight alkalinity, such as that caused by borax in the finishing, inhibits the coloring, which is possible only in neutral or acid fabrics. Cf. *C. A.* **15**, 600. CHAS. E. MULLIN

Comparative hygroscopic properties of certain textile fibers. ALBERT SCHEURER. *Bull. soc. ind. Mulhouse* **87**, 129–35(1921).—Const. wt. of fibers is attained in air heated to 110–120°. The object of this study was to det. the variations in wt. which samples of cotton, wool and silk undergo along with the daily variations in the relative humidity of the atm. The expts. were performed upon samples having an absolute wt. of 100 g. For cotton, 75/26 white Alsatian was used, for wool, muslin de lain with fat removed, and for silk, white Chinese pongé. The samples properly protected were suspended before a window, open day and night, and weighed from time to time. In a given instance the water absorbed was for cotton 8.1%, wool 15.4 and silk 10.8. With a different hygrometric state, the increase or decrease in the per cent of water absorbed by one fiber can be used to calc. the percent of water absorbed by the other two Samples ex-

posed to steam at 99.4° and 742 Bar. absorbed water in amts. proportional to those exposed to cold atm. L. W. RIGGS

Faults in fabrics due to chemical causes. D. K. COLLEDGE. *Am. Dyestuff Rep.* 9, No. 1, Sec. 2, 18–9(1921).—A paper read before the South of Scotland Section of the British Textile Institute. The principal faults of chem. origin are classed as those due to (1) poor oils, (2) defective scouring and bleaching, (3) dyeing and finishing. The first two factors cause oil stains, poor dyeings, inability of the dye to be taken up by the fiber, and tendering of the material. The SO_2 bleach gives rise to fading and color bleeding in the milling. The faults of dyeing are uneven results, tendering, bad penetration and loose colors. S. D. KIRKPATRICK

The by-products of wool scouring. JOHN W. RUSSELL. *Am. Dyestuff Rep.* 9, No. 1, Sec. 2, 11–4(1921).—The history of the wool-scouring industry and the fundamental chem. and physical principles of the processes are discussed. The 2 principal methods for recovering grease from wool-scouring liquors, *viz.*, the older "acid-cracking" and the newer centrifugal processes, are compared. S. D. KIRKPATRICK

Valuation of Turkey red oils (ANON) 27.

Dyes. W. J. POPE and SCOTTISH DYES, LTD. Brit. 162,687, Sept. 27, 1919. *N*-Dihydroanthraquinoneazine or its derivs. is prepd. by fusing 2-aminoanthraquinone or its derivs. with fused KOH in the presence of a salt of an org. acid, *e. g.*, K formate, tartrate or acetate, which is miscible with the fused alkali. An inert solid or liquid diluent may be present; and an oxidizing agent, such as $KClO_3$, may be added.

Disazo dye. T. M. SUSEMIHL. U. S. 1,378,388, May 17. A disazo dye, the Na salt of which is a greenish to brownish black powder sol. in H_2O, which dyes cotton, wool, silk or other fibers reddish shades which can be developed to blues and blacks, is formed by the diazotization of *p*-aminoacetanilide or of *p*-nitroaniline, coupling the diazo compd. with *m*-amino-*p*-cresyl methyl ether, rediazotizing, coupling with "I acid" and saponifying or reducing.

Dyeing apparatus. C. H. ROBBINS. U. S. 1,378,618, May 17.

Dyeing cellulose acetates. R. CLAVEL. U. S. 1,378,443, May 17. Cellulose acetates are dyed with solns. contg. a weak acid such as formic acid and sol. chlorides such as $ZnCl_2$ or NaCl which serve together with glue as foam producers and promoters of dye absorption.

Precipitating acid colors. A. LENDLE. U. S. 1,378,418, May 17. Acid colors such as "acid green," "patent blue" or "acid violet" are pptd. to form lakes by use of $BaCl_2$ or Pb acetate together with a phosphotungstate or phosphomolybdate or similar compd.

Bleaching fabrics. J. KERSHAW. Brit. 162,198, May 19, 1920. The fabric is passed through a dil. soln. of H_2O_2 contg. a trace of NH_3. It is then squeezed out and allowed to rest for a time, after which it is washed with an alkali soap. It is next passed through a soln. of $Na_2S_2O_4$ known to the trade as "Hydrosol," to which a trace of H_2SO_4 is added for some fabrics, squeezed out, rested for a short time, again washed, and then dried. Both solns. are used unheated, and are contained in baths through which the fabric is passed in piece form under submerged or partially submerged rollers.

Finishing fabrics. H. FORSTER. Brit. 162,627, Apr. 30, 1921. Transparent silky effects are produced on cotton and mixed fabrics by treating them first with a weak acid, then with a more concd. soln. of the same or another acid, and finally mercerizing. The acid may be replaced by known substitutes. Thus, the fabrics may be treated under tension first with H_2SO_4 of 49–50½° Bé. for 1–3 min., and may be then washed and dried, and next treated for 3–5 sec. with H_2SO_4 of 52–54° Bé., and finally mer-

cerized, while stretched, with a lye of 36–40° Bé. The H_2SO_4 may be replaced by H_3PO_4, HCl or HNO_3, or by a soln. of $ZnCl_2$ or $Cu(NH_3)_4O$, and figured effects may be obtained by subjecting only certain parts of the fabric to one or all of the treatments, a known printing process being used.

Fabrics impermeable to hydrogen. V. C. RICHMOND. U. S. 1,378,804, May 17. Superposed layers of rubber, gelatin compn. and nitrocellulose compn. are employed for rendering ballonnet cloth or similar fabrics but slightly permeable by H.

Scouring wool. R. M. POOLE and H. F. DAVIS. U. S. 1,377,790, May 10. See Can. 203,172 (*C. A.* **14**, 2992).

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Discussion of the Pfund paint gage. HENRY A. GARDNER AND P. C. HOLDT. *Paint Mfgrs. Assoc. U. S., Circ.* No. **132**, 4 pp. Aug. 1921.—The operation, and the results obtained by the use of the paint gage (*C. A.* **15**, 2988), are given. The instrument measures film thickness to an accuracy within 25% when applied to fairly smooth surfaces. Its most important application will no doubt be for gaging the thickness of coatings applied with a spray gun. Illus. F. A. WERTZ

Metal powder paint tests. HENRY A. GARDNER. *Paint Mfrs. Assoc. U. S., Circ.* No. **130**, 12 pp. July 1921.—The more ordinary grades of varnish are not satisfactory for making Al paints to be used for exterior work. The use of liquids of high acid values may cause hardening in the can and the formation of H with a resulting bulging of the containers. Extensive exposure tests on Al paints show that Al powder in raw or boiled linseed oil, or in spar varnish vehicles gives excellent results. Powder of 300 mesh is preferable if the paint is to be used for spray application. Nitrocellulose vehicles give paints very lacking in durability; aceto-cellulose vehicles give somewhat greater durability but are far inferior to oil or varnish. Unpolished Al powder gives results practically identical in luster and durability with the polished powder. With linseed oil vehicles, a paint contg. 30% pigment, and with spar varnish, a paint contg. 20% pigment, gave best results. Since Al powder retards the drying of raw oil, it is advizable to use boiled oil. The condition of the exposure panels and of the paint in the containers after storage for 9 mos. is reported in detail. Panels coated with red lead, blue lead, and Zn dust were included in the exposure as control tests. Illus. F. A. WERTZ

Two-year exposure results on Atlantic City panels. HENRY A. GARDNER. *Paint Mfgrs. Assoc. U. S., Circ.* **129**, 9 pp. (July 1921).—Results of the inspection of panels coated with various paint coatings after 2 yrs. exposure, are tabulated in detail. Metal panels coated with high grade linseed oil paints contg. such pigments as red lead, basic Pb chromate, etc., are still in good condition; as are also wooden panels coated with Pb-Zn paints, Fe_2O_3 paints, and with those contg. certain mixts. of TiO_2-$BaSO_4$-ZnO-Asbestine, and of lithopone and ZnO. The tests show the absolute necessity of painting black Fe sheets and tinned roofing plates to protect them from corrosion. Some new panels painted with Sb_2O_3-ZnO mixts. were exposed. Cf. *C. A.* **14**, 3802. F. A. WERTZ

Efficiency in the manufacture of linoleum. FELIX FRITZ. *Chem. Ztg.* **45**, 409–11 (1921).—F. reviews the methods of linoleum manuf. and makes general suggestions on increasing production, such as the utilization of heat from batches of boiled linseed oil instead of merely allowing them to cool in the kettle; greater forcing of oxidation of linseed oil on the festooned cloths so that a greater no. of coats of oil per day may be applied; use of a glycerol sized cloth from which the linoxyn layer may be stripped and the cloth used again; capacity loading of the cookers and mixers in the prepn. of linoleum cement; saving of power required for mixing, by heating the cement; stacking

of the finished linoleum in the drying room in a loosely wound roll and drawing warm air through it; etc. F. A. WERTZ

Artificial resins. A. TSCHIRCH. *Seife* **44**, 288–9(1921); *Chimie & industrie* **6**, 88(1921).—Review of the various sources of synthetic resins: aldehyde resins, methylene-phenol resins, various formaldehyde resins, coumarone resins, and miscellaneous resins. A. P.-C.

The high-temperature organism of fermented tan bark (GREIG-SMITH) **11C**. Abnormal iodine values (MACLEAN, THOMAS) **2**.

27—FATS, FATTY OILS AND SOAPS

E. SCHERUBEL

Solvent extraction in the vegetable oil industry. J. H. SHRADER. *Chem. Met. Eng.* **25**, 94–100(1921).—This article discusses: the principle involved in the solvent extn. of oil from vegetable materials, the com. development of the industry, stationary and rotary types of extractors with illustrations, principal solvents, economic considerations, and uses of products obtained. It is often stated that products obtained by solvent extn. are not comparable with those yielded by expression; but while extd. products are usually of high color and contain traces of solvent, it is also true that extd. products have been produced free from such objection. Extd. oils can often be refined to compare with expressed grades. The chief role of the extn. plant in the vegetable oil industry has been to work up off-grade residues, damaged seed, leather scraps and materials of no other value than their oil content. In Europe, however, these extn. products are used for human food; and in this country the meal is beginning to find a market as stock food. E. SCHERUBEL

Solvent extraction for vegetable oils. H. J. POOLEY. *Chem. Age* (London) **4**, 724–5(1921).—This is a summary of a paper given in connection with the International Rubber Exhibition. The points discussed are freight, final market, quality of oil, packages, manufg. facilities, fuel and power, special supplies and the extn. process. The claim is made that the Scott system is the most up-to-date system and plant for oil extn. by solvents. E. SCHERUBEL

The cultivation of oil-containing seeds and the oil industry of the Dutch East Indies. ANON. *Olien en Vetten* **5**, 524–5; **6**, 34–5, 44–5(1921).—A general review in which the cultivation, yield, and grading of oil seeds and the economics of the oil industry in the Dutch East Indies are considered at length. NATHAN VAN PATTEN

Olive refuse after extraction by carbon disulfide. P. E. VITORIA. *Anales soc. quim. Argentina* **7**, 317–34(1919).—The refuse left after two pressings and extn. by CS_2 is suitable for *fertilizer* as it is rich in N, K, and phosphates. Contrary to popular belief it may also be used as a *cattle food*. It should be finely ground to prevent injury to the intestines by large sharp pieces of broken seeds. Exptl. data on the products obtained by the destructive distn. of the refuse are also given in the article. L. E. GILSON

Fat and oil industry in Russia. ANON. *Bull. mat. grasses inst. colonial Marseille* 1918, No. **1**, 32–5; *Bull. Agr. Intelligence* **10**, 1000–3.—Statistics give the relative production, imports and exports of the more important animal and vegetable fats and oils for 1913 and 1917. The figures are official for 1913, estd. for 1917. C. C. DAVIS

The determination of the unsaponifiable matter in fats and oils using Halphen's method. V. VESELY AND J. KOPECNY. *Chem. Listy* **15**, 161–4(1921).—Halphen's method is based on the soly. of the fatty sulfoacids and sulfoglycerides in concd. H_2SO_4, on the insoly. of the mineral oils in this acid and also on the soly. of the latter in CCl_4, petroleum ether, or $CHCl_3$. In these solvents the sulfo derivatives are insol. in the

presence of H_2SO_4 (Halphen, *Rev. phys. et chim.* **1898**, 295). The method, as stated originally, gives inaccurate results because the solvent always contains not only the unsapon. matter and the residual H_2SO_4 but also considerable amts. of fatty acids. Filtration over bone char fails to remove the fatty acids. V. and K. propose washing the petroleum ether soln. with a 5% caustic soda soln., then with water and finally with 50% alc. Although this procedure does not remove the soap completely, however, the results are lower than those obtained by the Spitz-Hoenig method which indicates that the concd. H_2SO_4 not only reacts with the fats but sulfonates also a considerable amt. of the unsapon. matter, preventing its soln. in the petroleum ether. The accuracy of this method depends on the composition of the unsapon. matter since concd. H_2SO_4 sulfonates to a certain extent any cholesterol or phytosterol present. JOHN M. KRNO

Valuation methods of analysis for Turkey red oils. ANON. *Chem. Ztg.* **45**, 560–1 (1921).—Volumetric detn. Ten g. of high % Turkey red oil or 20 g. of low % are weighed into a 100 cc. beaker, dild. with 25 cc. H_2O and transferred to a Büchner fatty acid detn. app. Next 30 cc. of concd. HCl are added and the soln. is heated 20 min. The app. is filled to the graduated tube with concd. NaCl soln. and placed in a boiling H_2O bath for 15 min., when the vol. of fatty acids is read. The vol. of fatty acids times the sp. gr. of the fatty acids at 99° gives the wt. of fatty acids contained in the Turkey red oil. This multiplied by 10 or 5 (according to original wt. taken) gives the % of fatty acids in the red oil. Gravimetric method. About 10 g. of the oil are accurately weighed into a porcelain dish and then dissolved in 50 cc. H_2O and 15 cc. concd. HCl added. When the fatty layer is clear (about $^1/_2$ hr.) 10,000 g. of wax are added and the 2 mixed when melted. After standing $^1/_2$ hr. the mixt. is cooled and the cake sepd., washed, and melted again with distd. H_2O. After cooling and sepn. of the cake it is dried $^1/_2$ hr. at 105 to 110°. The difference in wt. between the dish plus wax plus fat and the dish plus wax = wt. of fatty acids. E. SCHERUBEL

The determination of the oil content of oleaginous seed. R. BIAZZO. *Bull. Orto Botan. Univ. Napoli* **6**, 75–9(1921).—The sample is ground and the flour obtained (about 100 g.) mixed in a mortar till homogeneous. A sample of this is taken (enough to yield not more than 2 g. oil) and triturated with 3 times its vol. of anhydrous $CuSO_4$. This is then ground with enough sand to give a friable mass which is placed in the extn. thimble and covered with anhydrous Na_2SO_4 previously used to clean the mortar and pestle and finally with absorbent cotton. When the extn. is completed the oil is filtered into a tared flask containing pumice, dried at 105° air being occasionally blown over it, and finally weighed. ALBERT R. MERZ

Estimation of resin acids in fatty mixtures. DAVID MCNICOLL. *J. Soc. Chem. Ind.* **40**, 124T(1921). *Volumetric method.*—About 2 g. of the mixt. are dissolved in 20 cc. of a 4% soln. of β-naphthalenesulfonic acid in dry MeOH and heated under a reflux condenser for 30 min. A blank expt. with 20 cc. of the sulfonic acid soln. is made at the same time. The best results are obtained by heating the flasks on an elec. plate. The contents of both flasks are then cooled and titrated with 0.5 *N* MeOH-KOH soln. *Gravimetric method.*—The neutralized soln. obtained above is employed. The contents of the flask are transferred to a separatory funnel, the vol. is noted and the flask washed out with an equal vol. of H_2O made slightly alk. with KOH. After shaking, the mixt. is extd. with an equal vol. of a mixt. of ether and petroleum ether. Sepn. is immediate. The small amt. of insol. soap is drawn off with the soap soln., which is extd. twice in similar fashion. The united exts. are washed with a little 50% alc. and the washings added to the resin soap soln., which is then acidified and extd. twice with ether. A no. of mixts. of known compn. were examd. by the methods described; the errors in the volumetric method varied between −0.22 and −0.56% and in the gravimetric method between −0.38 and + 0.35%. Two tables are given. The method detailed above

eliminates a fault of the Twitchell method, *viz.*, decompn. of resin acids with the production of water-sol. acids of lower mol. wt. E. SCHERUBEL

Notes on the oil from Cynara cardunculus. E. H. DUCLOUX. *Anales soc. quim. Argentina* **8**, 410–2(1920).—The plant is a common weed in the Argentine Republic. The data obtained from a complete physical and chemical examn. of the oil expressed from the seeds are given. The oil closely resembles cottonseed oil in its properties. L. E. GILSON

Characteristics and utilization of beech nut oil. H. B. *Mat. grasses* **13**, 5860–1 (1921).—The oil content of beech nuts varies from 14 to 22%. The consts. of the oil are: d_{15} 0.9205, I no. 104.4, Br no. 0.652, heat evolved with H_2SO_4 +65°, polariscope reading −0.8° in saccharimeter degrees, refractometer reading +16.5 to +18°. The oil is edible and keeps without change for a long time. The cake from the nuts gave the following analysis: decorticated cake: H_2O 12.5%, oil 7.5%, nitrogenous matter 37.1%, non-nitrogenous ext. 29.7%, cellulose 5.5%, ash 7.7%; non-decorticated cake: H_2O 19.1%, oil 8.34%, nitrogenous matter 18.15%, non-nitrogenous ext. 28.39%, cellulose 20.89%, ash 5.13%. The non-decorticated cake is not suitable for cattle food as it is poisonous. E. SCHERUBEL

Sakoa oil from Madagascar. HENRI JUMELLE. *Mat. grasses* **13**, 5854–5(1921).—Sakoa is the name given to *Sclerocarya caffra*. The fruits are drupes and have an acid pulp owing to the presence of citric acid. The seeds contain 56% of oil having the following consts.: d_{15} 0.9167, n_{10} 1.460, sapon. no. 193.5, I no. 76.6, R.-M. no. 0.1, Polenske no. 0.45, unsapon. matter 0.6%, m. p. of fatty acids 25°. The oil is non-drying and is suitable for soap making. E. SCHERUBEL

Grape oil from the Canadian vine (Vitis hederacea). ANON. *Boll. assoc. ital. piante med. aromat.* **2**, No. 4, 56–9; *Bull. Agr. Intelligence* **10**, 1004–5(1919).—Two oils were extd. (1) from the pips, a dark yellow or green oil with sweet taste and nutty odor, d_{15} 0.9215, n_{15} 1.4778, sapon. no. 189.2–189.6, I no. 131.4–141.6, fixed fatty acids 93.97%, volatile fatty acids 0% and non-saponifiable 1.44%. The total fatty acids have I no. 144.6 and mean mol. wt. 281.2. Solid fatty acids consisting chiefly of palmitic acid do not exceed 3%, have a mean mol. wt. of 261.4 and m. 57.6°. The liquid fatty acids are chiefly oleic and linoleic acids, with I no. 148.8–149.9. (2) From the pulp and skin was extd. an olive green soft pasty oil with astringent taste and pleasant odor, turning rancid in the air, n_{15} 1.4722, sapon. no. 192.3–193.3, I no. 90.3, fixed fatty acids 94%, volatile fatty acids 0% and unsaponifiable 1.67%. The total fatty acids have I no. 94.4–94.6 and mean mol. wt. 278.8. The solid fatty acids are about 10% of the pulp and skin oil, chiefly palmitic acid. The liquid fatty acids are mostly oleic and linoleic acids with I no. 110.2. C. C. DAVIS

Composition of holyhock seed and oil. R. S. HILTNER AND L. FELDSTEIN. *J. Ind. Eng. Chem.* **13**, 635(1921).—The hollyhock belongs to the same family as the cotton plant and its oil gives a strong Halphen and Becchi test and like cottonseed oil the Halphen test is made negative by heating for 10 min. at 250°. The seeds analyze as follows: H_2O 4.4%, ash 6.9%, ether ext. 11.9%, crude protein 21.2%, crude fiber 25.6%, starch 9.1%. The oil shows the following consts.: n_{25} 1.4722, $d_{15.6}$ 0.9275, I no. 119.0. E. SCHERUBEL

Ukuhuba fat. D. HOLDE AND W. BLEYMANN. *Z. deut. Oel-Fett-Ind.* **41**, 401–3, 419–21(1921).—This fat is from the seeds of *Myristica becuhyha*, black, wrinkled seeds, weighing 1.093 g. and yielding 64–70% fat. The fat contains mainly myristin with about 10% olein and 7.7% resinous matter, which is insol. in petroleum ether. The fat is of light yellow color, easily turning brown when extn. or pressing is prolonged. The com. fat forms a white crust on its surface; not so the lab. extd. fat. A drop of concd. H_2SO_4 produces a fuchsin-red coloration, especially the resin extd. from the fat.

When the fat was injected into the abdominal cavity of guinea pigs or rabbits, the animals died within 7–10 days of inflammation of the diaphragm. The resinous body is dark brown; its m. p. lies above 100°, acid no. 105.5, sapon. no. 195.3, unsapon. 3.9%; 9.8% of its acids are sol. in petroleum ether, 44.3 insol.; the remaining 42% were not detd. but they formed an insol. salt with KOH; I no. 25.3; they increase the n_D. The consts. of ukuhuba fat and its acids are as follows: m. p. by different observers 39 to 43°, solidification p. 32 to 40°, n_{10} 50.1 to 61.6, % free fatty acids 8.8 to 18.6, Hehner no. 93.4, sapon. no. 215.1 to 220.3, neutralization no. of the fatty acids 229, % of unsapon. 0.1 to 3.9, I no. 12.8 to 14.1, I no. of the fatty acids 9.5, R.-M. no. 1.7, Polenske no. 8.0, mol. wt. of the fatty acids 245. On account of its brown color the fat is not suitable for soap making. P. ESCHER

Distillation and grading of fatty acids. JOHN W. BODMAN. *Chem. Age* (N. Y.) **29**, 263–6(1921).—The operation of a typical Garrigue distn. plant is described. At the beginning of operation the still is charged with 15,000 lbs. of fatty acids and the temp. raised to about 450° F. The rate of distn. is gradually increased by the introduction of superheated steam until from 1500 to 2000 lbs. per hr. are distd. The temp. of the cooling H_2O when the still is operating at max. capacity should be 90 to 100° F. The still and superheater furnaces should be fired uniformly in order to maintain uniform temps. and even distn. About 100 lbs. of coal per hr. per still are required for the still and superheater furnace. When feeding black fatty acids to the still from 50,000 to 125,000 lbs. of stock can be fed before running down to tar in the case of garbage grease of low grade animal fats and 50,000 to 80,000 lbs. in the case of cottonseed fatty acids. The yield of double distd. fatty acids from cottonseed foots is about 85%, and 12% pitch. Garbage grease fatty acids yield about 90% and 6% pitch. The higher the split the higher the yield of distd. fatty acids In the most modern installations rotary vacuum pumps are used for pulling dry vacuum off a countercurrent barometric condenser. Improvements have also been made in the design of the steam distributing system inside the still together with design of furnace work which enables even distribution of heat over the still bottom. There has recently been designed a special separator which was placed on the vapor line leading from the still to the first surface condenser to det. whether coloring matter is carried over with the fatty acid vapors in the form of a true vapor or as mechanical entrainment. Expts. indicate that coloring matter can be removed mechanically. There are no standards for grading fatty acids at the present time. One of the first steps to decide is whether the color of distd. fatty acids should be judged by reflected or transmitted light. It may be said that a color reading of 35 yellow and 6 red on the Lovibond color scale read through a 1 in. column of liquid fatty acids will meet the av. com. requirement. Also in *Cotton Oil Press* **5**, No. 3 41–5(1921). E. SCHERUBEL

The bleaching of oils, fats and waxes. STEINAU. *Chem. Ztg.* **45**, 559(1921).—German-manufd. bleaching earths are said to give better results than the natural imported product, and they have the additional advantage of retaining less oil. In the case of olive oil the operation is carried out as follows: The oil is heated to 38 to 40°, 3 to 5% of "Silitonit F" is added and the oil is filtered. Green sulfur oil is acid-washed with H_2SO_4 before bleaching. Linseed and rape oils are bleached water-white with 5 to 10% of Silitonit F and S. Light mineral oils of d_{15} 0.850 give a white oil with 3 to 5% of bleaching earth; heavy mineral oils of d_{15} 0.950 are changed from dark brown to a wine yellow with 5 to 10% of earth using a temp. of 120°. E. SCHERUBEL

Commercial saponification of fats. EMM. POZZI-ESCOT. *Chimie & industrie* **5**, 326(1921).—P.-E. uses a 1.5 cu. m. autoclave and establishes an intense circulation by means of a powerful centrifugal pump which takes the liquid at the bottom of the autoclave and projects it against a rotating atomizer at the top of the autoclave. With 500–

600 kg. of cottonseed oil and 100 kg. of water the temp. is raised to 180–90°, and the pump is then started. Saponification is nearly complete in less than 1 hr. Certain salts, and especially Ni formate, considerably hasten the reaction. With the same app. when the circulation system was not used, saponification of the same amt. of oil in the presence of 2% ZnO by passing through steam at 9–10 atm. required over 10 hrs. By using this intense circulation and merely having the fat in contact with the steam, but dissolving the glycerol in H_2O as it forms, a much higher concn. of glycerol is obtained than by the old process. A. P.-C.

Sodium acetate as a hardening agent in soap making. LEONARD M. LIDDLE. *Chem. Age* (N. Y.) **29**, 266(1921).—Discussion of patent no. 1,377,843, granted May 10, 1921. The addition of varying proportions of Na acetate or lactate makes possible imparting to the soap the added detergency and firmness given by the use of the alk. materials generally incorporated, but with none of the deleterious qualities inherent in them. In the manuf. of transparent or cold-made soaps, the addition of Na acetate may be made by adding AcOH in amt. sufficient to neutralize the excess alkali. The final incorporation of 1 or 2% of Na acetate or lactate effects the desired hardening without detracting from the transparency. Na lactate is superior to Na acetate in promoting transparency. If too much water is added during the manufg. process so that the soap will not set, it can be readily made to harden by the addition of a small amt. of Na acetate. A detergent such as soap powder or flakes may contain Na acetate with advantage. The softening effect of Na resinate in all rosined soaps is readily neutralized. E. SCHERUBEL

Determination of fatty acids in soaps by the wax cake method. P. ABEL. *Z. deut. Oel-Fett-Ind.* **41**, 437(1921).—A. calls attention to the formation of permanent gas bubbles on the surface of the fatty acids when paraffin or wax is added for the purpose of solidification. He removes them by placing a flask with hot H_2O on the vessel contg. the acids, and by gently heating the sides of the vessel with a flame the heat bursts the bubbles. P. ESCHER

The wax of Gueriniella serratula Fabr. O. PRANDI. *Staz. sper. agrar. ital.* **53**, 309–16(1920).—The crude wax contained 23.84% of ether-sol. fatty substances which formed a solid reddish yellow mass of disagreeable, strongly rancid odor, and with the following properties: d_{15}^{15}, 0.874; m. p., 54–56°; f. p., 49–51°; refractometric degree (Zeiss butyro-refractometer), reduced to 40°, 75; acid no., 52.75; free acid (as oleic acid), 26.5%; sapon. no., 179–180; Hehner no., 69.5; I no., 41.73; ester no. 127.27. The ether-insol. waxy substance, recrystd. from C_6H_6, formed minute white scales of silky luster and unctuous feel; m. p. 88–89°; f. p., 88°; d_{15}^{15}, 0.985; refractometric reading, 48.7 (reduced to 40°); sapon. no., 69; acid no., 0; ester no., 69; very sol. in hot C_6H_6, $CHCl_3$ and CS_2; quite sol. in cold $CHCl_3$ and CS_2; slightly sol. in cold C_6H_6, hot petroleum ether, hot C_2H_5OH and Et_2O; Hehner no., 53.33. Contains no unsatd. compds. and no cholesterol. It is formed chiefly of myricyl myricylate and small amts. of esters of cerylic alc. and unidentified acids. Myricyl acetate was found to have a m. p. of 70° instead of 75° as stated by some. ALBERT R. MERZ

The utilization of the carnauba-wax palm. CLEMENS GRIMME. Inst. f. angew. Bot., Hamburg. *Pharm. Zentralhalle* **62**, 249–57(1921).—The fruit of the carnauba-wax palm is edible and the roasted seeds are used as a coffee substitute. The flesh contains H_2O 15.04, protein 5.46, fat 6.25, N-free ext. 64.32, crude fiber 5.81 and ash 2.95%. The seeds contain H_2O 10.55, protein 6.89, fat 13.65, N-free ext. 63.29, crude fiber 4.07 and ash 1.55%. The sugar in the flesh is glucose. The seed-oil has a d_{15} 0.9483, m. 28.3°, n_{40} 1.4291, acid no. 2.64, sapon. no. 221.5, ester no. 218.9, I no. 23.3 and a Reichert-Meissl no. 4.2. The analysis of samples of carnauba-wax were reported.

H. A. SHONLE

Extraction of candelilla wax. José de Bano. *Rev. agr.* (*Mexico*) **5**, 822–4(1921).—A description of recent attempts to prep. candelilla wax of suitable commercial quality in Mexico, including the proper method of collecting the plants, extg. the wax with boiling water, bleaching and drying. M. R. Schmidt

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Soaps medicated with corrosive sublimate (Issoglio) **17**. Abnormal iodine values (Maclean, Thomas) **2**. The manufacture of starch, glucose and by-products (Williams) **28**.

Andés, Louis Edgar: **Vegetablische Fette und Oele.** Wien and Leipzig: A. Hartleben's. M 20. For review see *Z. öffentl. Chem.* **27**, 130(1921).

Fischer, H.: **Der Seifensieder.** Leipzig: Verlag von Bernh. Friedr. Voigt. 240 pp. M 42.50. For review see *Seifensieder-Ztg.* **48**, 247(1921).

Kanthack and Goldsmith: **Table of Refractive Indices. Vol. II: Oils, Fats, and Waxes.** London: Adam Hilger, Camden Road. £1.5. For review see *Rev. Ping index tech.* **19**, 40(1921).

Schrauth, Walter: **Handbuch der Seifenfabrikation.** 5 ed. Berlin: Julius Springer. M. 120. For review see *Oesterr. Chem.-Ztg.* **24**, 71(1921).

Catalytic hydrogenation of fats, etc. E. R. Bolton. Brit. 162,370, Jan. 26, 1920. A catalyst for use in the hydrogenation of fats or oils consists of Ni wool which has been activated by the action of an acid such as HNO_3 upon its surface followed by conversion of the layer of Ni salt to oxide and reduction in H. The reaction chamber is packed with the activated Ni wool and the oil and H are passed through in countercurrent. After use the catalyst is regenerated by first removing Ni soaps by washing with the hot oil, then removing the oil by solvents and finally heating in H. According to the provisional specification, the Ni wool may be activated by alternate oxidation and reduction, the catalyst may be electrically heated, and a number of reaction vessels may be arranged in series.

Catalytic hydrogenation of fats, etc. E. R. Bolton and E. J. Lush. Brit. 162,382, Jan. 27, 1920. In the catalytic hydrogenation of fats or oils, mono- or diglycerides of the fatty acids are added at the start in amt. sufficient to neutralize free fatty acids either present in the oil or formed therein by hydrolysis during the hydrogenation; contamination of the Ni catalyst by Ni soaps is thereby avoided and its active life prolonged.

Catalyst for hydrogenating oils. C. Ellis. U. S. 1,378,336, May 17; Brit. 162,038, Jan. 14, 1920. A catalyst for hydrogenation is formed by mixing an org. Ni salt such as Ni formate, acetate or stearate with a petroleum or fatty oil and heating the mixt. *in vacuo* to a temp. of about 250° in order to decompose the salt. U. S. 1,378,337 also relates to a catalyst made by thus decomposing Ni oleate in oil. U. S. 1,378,338 relates to production of catalysts by reducing a mixt. of salts of Ni, Co and Cu, *e. g.*, the oleates, in oil. A current of H may be passed through the mixt. during the heating.

Soap. L. M. Liddle. U. S. 1,377,843, May 10. A neutral or nearly neutral soap is mixed with NaOAc, Na lactate or other alkali metal salt of a lower fatty acid in order to improve the hardness or detergent properties of the soap.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Contributions to the history of sugar. E. Wiedemann. *Deut. Zuckerind.* **46**, 302–3(1921).—Translations are given from Ibn Gazla (about 1100 A. D.), concerning

the prepn., nature and properties of cane sugar and of "uschar"-sugar (-gum), and from Abu'l Fazl (about 1600 A. D.) on the cultivation of cane and the prepn. of arrak.

F. W. ZERBAN

Compounds between sugars and salts. H. C. PRINSEN-GEERLIGS. *Arch. Suikerind.* **29**, 567–71(1921).—The failure of Helderman to obtain such compds. (*C. A.* **15**, 322, 2010) may be due to shortcomings of the method used by him. Their actual existence has been amply proved by Maumené and others, and confirmed by P. In fact, P.'s theory of the formation of molasses is largely based on this fact. F. W. Z.

Sugar-salt compounds. W. D. HELDERMAN. *Arch. Suikerind.* **29**, 571–4(1921).—Reply to Prinsen-Geerligs (cf. preceding abstract). H. does not doubt the existence of compds. between sugars and salts under certain conditions, and his own expts. neither prove nor disprove it. He has demonstrated, however, that in all cases studied by him there were no compds. formed which at 30° were stable as solid phase in equil. with their satd. soln.

F. W. ZERBAN

Decomposition of sucrose in solution by atomization. W. D. HELDERMAN AND C. SIJLMANS. *Arch. Suikerind.* **29**, 495–500(1921); *Intern. Sugar J.* **23**, 403–5.—This work was undertaken to test by expt. the hypothesis of Schweizer (*C. A.* **14**, 858), supported by Van Ham and by Olsen (*C. A.* **14**, 858), but doubted by de Haan (*C. A.* **14**, 2274), that a sugar soln. when very highly dispersed in rapidly traveling vapor or steam is liable to undergo inversion and even complete decompn., leading to the formation of CO_2. Two special forms of app. were used, in one of which the sugar soln., heated to 90°, was atomized by compressed air and forced in this state to travel 2 and 4 m. resp. In the other app. the atomization was effected by a vacuum pump, and the whole expt. carried out under reduced pressure. No appreciable decompn. could be detected in either case, not even in the presence of invert sugar or of KCl. The conclusion is drawn that in factory practice no losses due to atomization need be feared.

F. W. ZERBAN

Decomposition of sucrose in solution by atomization. A. SCHWEIZER. *Arch. Suikerind.* **29**, 663–5(1921).—Reply to Helderman and Sijlmans (cf. preceding abstract). H. and S. did not make their expts. with cane juices, nor in an acid atmosphere as is often encountered in the vapor lines of the factory. Their negative results with pure sugars, in a neutral medium, do not justify their conclusion that in actual factory practice destruction of sugar by atomization need not be feared. Unknown losses may not always be caused by atomization, but before it can be definitely stated that they never are, the tests should be repeated under conditions more closely resembling factory practice.

F. W. ZERBAN

Continuous sampling of sugar liquors. WALTER L. JORDAN. *J. Ind. Eng. Chem.* **13**, 640–1(1921).—None of the methods hitherto used gives a truly representative sample as either collections are made periodically, or, if a continuous sample is taken, its quantity is not proportional to the liquor flow. J.'s device consists of a slot weir placed on top of a vertical overflow discharge pipe. The weir widens into a funnel from where the sample flows into a receiving vessel. The amt. of sample is approx. the same fraction of the liquor vol. passing at any one time, as the width of the slot is in relation to the entire circumference of the overflow pipe, and the depth of flow through the weir and the rest of the circumference is strictly the same. Where very large vols. of liquor are to be sampled, the first sample may be again reduced by means of a second weir.

F. W. ZERBAN

A neglected factor in sugar analysis. C. A. BROWNE. *Facts About Sugar* **13**, July 16, 50, 51, 55(1921).—B. confirms Vosburgh's findings that when a sugar is dissolved in water the solvent is no longer water, but water plus a certain part of the same sugar. B. gives exptl. evidence to show that variations in the polarization of sugar

depend upon other substances present. The bearing of this upon the Clerget divisor is shown in that the value of the negative component in the Clerget divisor is not dependent on the concn. of the invert sugar, as is generally assumed, but upon the fixed relationship between the water, acid, salts and other ingredients of the solvent in which the invert sugar is dissolved. The magnitude of the errors thus introduced and the proper correction for the divisor based on water content are indicated. Results of polarizations in the presence of NH_4Cl, instead of HCl, and tests with equal amounts of sucrose and dextrose are given as further evidence of the neglect of the factor of water concn. Also in *Louisiana Planter* **67**, 44–6(1921). N. KOPELOFF

A new system of colorimetric measurement for the sugar industry. V. SÁZAVSKY. *Listy Cukrovár.* **39**, 209–11(1921); *Z. Zuckerind. Čechoslovak. Rep.* **45**, 299–301(1921).—The introduction of vegetable decolorizing carbons has increased the importance of the measurement of the color concn. of sugar solns. Scheuer and Oleszkiewicz (*C. A.* **6**, 3338) failed to consider in their measurements that the color concn. is a function of the vol. of the soln. in question. Koydl (*C. A.* **11**, 2739) developed a system of measurement based on saccharan. The objection to this is that the adsorption power of boneblack and vegetable carbons towards saccharan is much less than towards the color substances in sugar solns. met with in practice. Staněk (*Listy Cukrovár.* 1916–17, pgs. 351, 367, 489, 503) isolated from molasses a nitrogenous substance of acid character which he named *fuskazinic acid*, the alk. salts of which form nearly $^1/_2$ of the color substance in molasses. 1 mg. of *fuskazinic acid* will give a color equal to 1° Stammer. S. proposes a method of color measurement based on this substance. Its application to the detn. of the adsorption capacity of carboraffin is given. JOHN M. KRNO

A new sugar refractometer. HANS SCHULZ. C. P. Goerz A.-G. Berlin. *Z. Ver. deut. Zuckerind.* **71**, 347–59(1921).—It is doubtful whether the figures for n of sugar solns., given by Krüss (*C. A.* **15**, 1827) are really closest to the actual values. They show differences up to 4 units in the 4th decimal place from Schönrock's figures which, according to the latter, are accurate to one unit in the 5th decimal. There is in fact no simple relation between n and the concn. of the soln. A close approximation of calcd. and observed values is arrived at by taking the av. of 2 values n_1 and n_2. n_1 is calcd. from the formula $n_1 = n_0 + p + bp^2 + cp^3 + dp^4$, where $n_0 = 1.33300$, $a = 0.0014646$, $b = 0.26563 \times 10^{-5}$, $c = 0.76042 \times 10^{-7}$, $d = -0.39663 \times 10^{-9}$, and p = concn. in % sugar. n_2 is found from the formula $\log (n_2 - a) = cp - b$, where $a = 1.14515$, $b = 726073$, and $c = 0.0032983$. The figures for dispersion, found in the literature, are not reliable either. A table is given showing the dispersion for various concns., under the assumption that $n_D - n_C$ and $n_F - n_D$ change linearly with the concn. The new instrument consists of a double prism similar to that used in the Abbe instrument, made of glass of low refractive index, in order to increase the sensibility. The effect of dispersion is nearly eliminated by a compensation prism made of Sendling glass 626/393 whose dispersion closely approximates that of water and of sugar solns., when cut at the proper angle. The app. differs from similar ones in that the compensation prism and telescope are mounted in a fixed position, while the measuring prism itself is rotated. The rotation is transmitted to 2 milled screw heads placed within easy reach of the operator. There are two scales, on a large disc right in front of the operator, one giving n, and the other % sugar in steps of 0.5%, so that 0.1% can easily be estd. The axis of the entire apparatus is nearly horizontal so that it can be read like a polariscope. The thermometer is mounted along the body of the instrument to prevent breakage. F. W. ZERBAN

Recording instrument for the automatic weigher patented by Adam. M. REVIUS. *Arch. Suikerind.* **29**, 551–2(1921).—The app. described by Vos (*C. A.* **15**, 2562) has the disadvantage that the Cu tube is liable to break from repeated bending. This may be overcome by passing the tube through the inside of the shaft which supports

the weigher. The recording instrument is best placed on the framework of the weigher, thus shortening the Cu tube. F. W. ZERBAN

Tables and formulas needed in connection with the boiling and working up of juices and run-offs in raw sugar manufacture, with explanations and examples. K. BARTSCH. *Z. Ver. deut. Zuckerind.* **71**, 267–322(1921). F. W. ZERBAN

Sulfitation and filtration of cane juice. E. BUDAN. *J. fabr. sucre* **62**, No. 29(1921).—An installation is described where the waste gases ordinarily allowed to escape into the air from the top of the sulfitation chambers are forced, by means of a steam injector, into a pipe ending in a number of perforated branches in the bottoms of the defecating tanks and utilized for stirring the contents of the tanks. Any SO_2 in the gases is thereby utilized. Incidentally the sulfitation chambers by this arrangement will operate under slightly reduced pressure, preventing loss of SO_2 through leaks. Filtration problems are discussed briefly. L. E. GILSON

The effect of press cake washing on the yield. TIEMANN. *Deut. Zuckerind.* **46**, 285(1921).—Reply to Müller (cf. *C. A.* **15**, 2561). It was proven long ago that the small amt. of non-sugars dissolved by prolonged washing has no effect on the yield. However that may be, the use of pieces of sheet metal or such like placed against the lower part of the cloths is not advizable, because they reduce the filtering area unduly. Centrifugal pumps are not to be recommended either. The pulsations of reciprocating pumps have, in fact, a favorable effect, shaking up the mud, and thus hastening filtration. They permit of better pressure regulation and flow control, while centrifugal pumps drive the mud into the cloth at the beginning, with unfavorable effect on the speed of filtration. F. W. ZERBAN

Tests with low-grade massecuites. W. D. HELDERMAN. *Arch. Suikerind.* **29**, 694–7(1921).—These tests were made in order to ascertain whether insulation of the tanks for crystg. low-grade massecuites would tend to lower the purity of the final molasses. Two of the tanks were imbedded in 8 in. of solid masonry and tightly covered, while two others were not so treated. The massecuite in one of the tanks was purged after 1 month, that from the other three after 2 months. Investigation of the sugar and molasses from the last three showed that the crystals from the insulated tanks were larger and that the percentage yield of sugar was higher. But since the purities of the original massecuites were not the same, no definite conclusions can be drawn. F. W. ZERBAN

Molasses from cane and from beet. TIEMANN. *Deut. Zuckerind.* **46**, 303–4(1921). Compds. between salts and sugars which, according to Helderman (*C. A.* **15**, 322, 2010) do not exist in Java cane molasses, certainly are present in beet molasses. They are combinations of the normal K and Na salts of polybasic organic acids, reacting alk., with carbohydrates which replace water of crystn. They are colloidal and cause the high viscosity of beet molasses. The acid salts of the same acids are crystalline, and have no water of crystn. This explains the difference between cane molasses which is always acid, and beet molasses which is carried alk. The sugar-salt compds. also explain the well-known differences in density found by direct detn. and by the double diln. method. The possibility of adding water to low grade massecuites without dissolving sugar is also due to the fact that it replaces sucrose combined with salts. If glucose is also present, it takes the place of sucrose in the combination before water does, and this is the cause of the salting-out effect of glucose on sucrose. F. W. ZERBAN

Fine grain in molasses. C. SIJLMANS. *Arch. Suikerind.* **29**, 659–62(1921).—Some expts. were made for the purpose of ascertaining whether the method of heating instead of diln., as proposed by Kalshoven (*C. A.* **14**, 860) and advocated by Dědek (*C. A.* **15**, 187) for beet molasses, was applicable to the detn. of fine grain in Java cane molasses. Four samples of molasses, of different origins, were tested, and it was found

in each case that heating in an autoclave at 100° gave lower results than diln. It was also proven by the addition of sugar crystals that the diln. method gives correct figures. The method of Dědek can, therefore, not be used on Java molasses. Refractometer readings are greatly facilitated by first shaking the molasses in a half-filled bottle to sat. it with air bubbles. The lighter and darker portion of the field are found to be reversed, but the contrast between them is greater. This contrast may be further increased by holding the finger over the lower part of the ground glass upon which the light falls. With these improvements it is possible to det. the fine grain to 0.2%. F. W. ZERBAN

Graphic determination of the steam consumption and steam economy in sugar factories. W. A. HATTINK. *Arch. Suikerind.* **29**, 531–50(1921).—It is shown how by graphic methods, which are explained in detail, the steam consumption of each station, particularly preheaters, evaporators, and pans can be detd. and controlled, and necessary economies and improvements indicated. F. W. ZERBAN

Further investigation on the causes of undetermined losses. J. S. DE HAAN. *Arch. Suikerind.* **29**, 555–67(1921); cf. *C. A.* **14**, 2274.—Ever since entrainment has been reduced to a minimum by the installation of proper catch-alls, an increase has been observed not only in the quantity of sugar produced, but also in that of the molasses. In fact, more molasses is obtained than was to be expected. This would mean that the non-sugars increase during evapn. and boiling, and this increase must be due to a decompn. of sucrose. It was the purpose of this investigation to det. the magnitude of this decompn. The plus production of molasses can readily be measured by weighing the sirup or juice, and the molasses. The amt. of sucrose decompd. is much more difficult to det., but it may be estd. on the basis of the assumption, which has so far not been proved, that one part of non-sugars is formed from one part of sucrose. For the campaigns of 1919 and 1920 the excess of molasses produced by several factories over that calcd. averaged 3% of the latter. From this it follows by a simple calcn. that the amt. of sucrose destroyed in the same factories during the same period averaged 0.38% of that in the juice. This is probably a minimum figure for sucrose destroyed. To this must be added the sucrose lost in the excess molasses produced, which amounts to 0.22%. The total loss of sucrose caused by chem. effects is therefore found to be 0.6% of that present in the juice. It may be objected that the decompn. products of sucrose are not molasses-forming, and simply replace sucrose. But Van der Linden's work (*C. A.* **14**, 859) shows that such is not the case. It remains to be shown that one part sucrose yields one part non-sugar. This assumption is strengthened by the fact observed in one of the factories where an undetd. loss was found during a certain period, amounting to 2263 piculs sucrose, and 1985 piculs total solids. The excess molasses produced was 442 piculs. The latter would mean a loss by decompn. of 250 piculs sucrose. Deducting this from the 2263 piculs, 2013 piculs is left, or almost the same as the loss in total solids. This would indicate that the sugar was lost as such, and as a matter of fact, the loss was due to faulty weighing of the sugar. Good automatic scales, carefully and regularly controlled, will probably help to overcome this source of loss.
F. W. ZERBAN

Sugar-cane experiments 1918–1920. Trinidad seedlings and test of varieties. J. DE VERTEUIL. *Bull. Dept. Agr. Trinidad and Tobago* **19**, Pt. 2, 66–80(1921).—Complete tabulated data comprizing wt. of stool, wt. of canes, analysis of the juice, including % extd., sp. gr., Brix, % sucrose, % *d*-glucose, % non-sugar, and quotient of purity with sucrose per gal. are given for 162 seedlings. Similar data are presented for about 80 varieties of cane. R. B. DEEMER

The manufacture of starch, glucose and by-products. R. H. WILLIAMS. *Can. Chem. Met.* **5**, 195–6(1921).—W. describes the handling of corn to effect sepn. of starch, glucose, the meal or feed, and corn oil. After removal of chaff and dirt, the corn is

steeped 1.5–2 days in 0.3% H_2SO_3 at a temp. of 60°, which effects the softening of the glutinous parts of the grain and prevents fermentation. From the steeps, the grain passes through a mill having two parallel plates revolving in opposite directions and carrying studs. The corn then passes through the germ separators, where the germs loosen and rise to the surface; they are removed by wooden paddles and carried to the shakers. The other portion of the kernel goes to a set of shakers and the squeezer where the starch and most of the gluten are washed through the bolting cloth while the fibrous portion (slop) passes over the ends of the sieves. The sepn. of starch, the varieties obtained and the manuf. of glucose and utilization of by-products are discussed. The cake or feed consists of the slop from the shakers, the oil cake from the oil press and the gluten liquor from the cone settlers. Sometimes the solid matter contained in the used steep water is also included. Corn oil is gaining favor as a soap oil. W. H. BOYNTON

Notes on fecula. A. REYCHLER. *Bull. soc. chim.* **29**, 311–6(1921).—*Fecula paste* prepared at about 100° is a suspension of highly hydrated swollen grains in a very dil. *amylase* soln. It is coagulated by solns. of iodine and of sulfates and jellified by alkalies and by salts and acids which are sol. in alc. and in water. It retrogrades spontaneously to *artificial amidon* which is probably purer *amylose*. When fecula is heated with water to 150°, it forms a colloidal soln. Malt ext. has only a slight effect on this material after it has been aged on ice for ten days but rapidly and completely liquefies the fresh starch. The aging renders the parietal material, which is rich in *amylopectin*, especially resistant. Amylose and amylopectin are probably polymers of the same substance. WM. STERICKER

Summary of the results of plot tests for cane culture in Java (KUYPER) **15**. Cellulose and other carbohydrate ethers (Brit. pat. 163,017–8) **23**.

RÖSSING, A.: **Frühlings Anleitung zur Untersuchung der Rohstoffe, Erzeugnisse, Nebenerzeugnisse und Hilfstoffe der Zuckerindustrie.** Braunschweig: Verlag. Fried. Vieweg & Sohn. For review see *Z. angew. Chem.* **33**, I, 40(1920).

Vegetable glue. F. S. WILLIAMS, G. B. PERKINS and J. B. B. STRYKER. U. S. 1,378,078, May 17. A vegetable glue suitable for gluing up veneers is formed of starch in soln. in about 3 times its wt. or less of H_2O, together with caustic alkali.

Vegetable glue. W. M. GROSVENOR. U. S. 1,378,105, May 17. A glue suitable for use with wood veneers is prepd. by dissolving starch without use of caustic alkali, in about 3 times its wt. of H_2O or less together with a substantially neutral solvent for starch cellulose such as Na_3PO_4, Na_3AlO_3 or basic Pb acetate.

Vegetable glue. W. M. GROSVENOR. U. S. 1,378,106, May 17. Modified starch uncombined with S is dissolved with about 4 times its wt. or more of H_2O together with NaOH or other alk. substance to form a glue suitable for use on wood veneers.

Vegetable glue. J. G. B. PERKINS and J. B. B. STRYKER. U. S. 1,378,128, May 17. Starch is dissolved with H_2O and NaOH or other alk. material to form a soln. of such viscosity that it flows through 2 in. pipes and can be spread by the usual glue-spreading machinery and the soln. is treated with NH_4Cl or $(NH_4)_2SO_4$ to neutralize it without materially decreasing its strength or spreadability. The glue thus formed is suitable for use with wood veneers.

29—LEATHER AND GLUE

ALLEN ROGERS

Certain characteristics of fresh steer hide. GEORGE D. MCLAUGHLIN. *J. Am. Leather Chem. Assoc.* **16**, 295–309(1921).—An investigation has been conducted with

the idea of studying the effects of certain acids, alkalies and salts on the swelling of fresh hide, *i. e.*, hide which has been removed from the animal's body not more than 30 min. The results of these expts. are tabulated. All of the acids employed had a swelling effect on the corium, the amt. depending upon (*a*) the character of the acid and (*b*) the concn. Org. acids, in concns. greater than 0.05 *N*, showed the greatest general swelling and mineral acids the least, while oxalic occupied positions midway between the two groups. If the corium was removed from the several acids, and soaked further in lactic acid, additional swelling was observed. All of the alkalies employed swelled corium, the amt. depending upon the same factors as in the case of acids. Chlorides of NH_3, K, Na produced the greatest swelling and chlorides of heavy metals, the least. Chlorides of Li, Mg, Ca occupied a middle position. The possibility of admixtures of heavy-metal salts with NaCl in salting hides is of importance, also their effect in soaks and limes. $HgCl_2$ must be used with care for disinfecting hides because of its effect upon the subsequent swelling of hides with acid or alkali. Lactic acid (0.05 *N*) swelled corium 53.3% but the subsequent total swelling was less when the corium had been first treated with chlorides. NaOH (0.05 *N*) swelled the corium 20.4%, but this figure was increased when the corium had been first soaked in certain concns. of some chlorides. Corium treated with sulfates usually swells less in 0.05 *N* lactic acid than that treated with chlorides and swells less in the subsequent bath of 0.05 *N* NaOH, with the exception of K_2SO_4. When fresh hide is allowed to stand for various periods before entering a satd. CaO soln., its swelling capacity is materially and progressively changed. H. C. PARISH

Chestnut-wood tannin. ROBERT W. GRIFFITH. *J. Am. Leather Chem. Assoc.* **16**, 327–32(1921).—A general discussion. A series of tests made on pure tannages of the chestnut wood, quebracho, oak bark, valonia and hemlock showed that the greatest tensile strength is possessed by the chestnut-wood tannage. H. C. PARISH

Tannin content of the fruit of Caesalpina melanocarpa. FIDEL ZELADA. *Anales soc. quim. Argentina* **9**, 129–36(1921).—See *C. A.* **15**, 1419. L. E. GILSON

Nitrocellulose and its solutions as applied to the manufacture of artificial leather. W. K. TUCKER. *J. Ind. Eng. Chem.* **13**, 623–4(1921).—T. discusses some of the specifications for nitrocellulose for use in the artificial leather industry and the 2 solvents most commonly used, acetone oils and AcOEt. The solns. usually used have a viscosity of 40 sec. Correction. *Ibid* 1082. C. J. WEST

A simple method for testing glue. D. R. FRAZER. *Analyst* **46**, 284–5(1921).—Pieces of pitch pine with the grain running lengthwise are cut to the dimensions of briquets used in testing cement. These are sawn through the middle and the ends sandpapered to an exact fit. On one of the ends there is spread 0.3 cc. of a 25 to 100 glue soln. at 50°, and the other piece quickly applied. The 2 pieces are held together by the pressure of a 2-in. rubber band for 24 hrs., and the briquet tested in the cement-testing machine in the usual manner. From the results on 10 samples F. suggests the following standards, the figures being tensile strength in lbs. per sq. in.: Good—over 300; medium—150 to 300; poor—less than 150. [Since the strength of a joint depends vitally on the pressure used in making it, this method is hardly of value even as a crude approximation. Some of the "abnormal" briquets which F. advizes neglecting, show a variation of over 300%. ABSTR.] JEROME ALEXANDER

HARVEY, ARTHUR: **Practical Leather Chemistry.** London: Crosby, Lockwood & Co. 15s net. For review see *J. Roy. Soc. Arts* **69**, 579(1921).

HARVEY, ARTHUR: **Tanning Materials, with notes on Tanning Extract Materials.** London: Crosby Lockwood & Son. 182 pp. 15s net. For review see *Chem. Age (London)* **5**, 34(1921).

Tanning hides. P. BRANDT and H. T. WILSON. U. S. 1,378,213, May 17. Partly prepd. leather containing tannin is treated with dissolved glue and tannin in the presence of an alk. compd. such as NaOH and oil and is afterward treated with an acid soln. *e. g.*, lactic acid or H_2SO_4, in order to fill, weight and waterproof the material.

Liming hides. R. C. R. MARKS. Brit. 163,109, Feb. 9, 1920. In a liming and unhairing process, the hide is first soaked in an aq. soln. weak in lime and mild in Na_2S, is then washed to eliminate the sulfide, being subsequently soaked in a stronger soln., of CaO only. A suitable construction is specified.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

The structure and synthesis of the caoutchouc molecule. S. C. J. OLIVIER. *Chem. Weekblad* **18,** 231–4(1921).—The literature is reviewed at length, accompanied by many references. NATHAN VAN PATTEN

The cold auto-polymerization of butadiene. C. HARRIES. *Gummi-Ztg.* **35,** 898(1921).—Several tubes of butadiene kept in the dark for 5 yrs. changed to a white brittle substance containing small particles of butadiene. This material was shown to differ from the analogous products of β,γ-dimethylbutadiene and of isoprene. There are, therefore, now known 3 entire series of polymerization products of the 3 chief butadienes, namely erytherin (butadiene), isoprene (β-methylbutadiene) and β,γ-dimethylbutadiene: (1) Cold polymerization products, (2) hot polymerization products, or normal rubbers, (3) abnormal rubbers obtained by means of Na without CO_2. A. L.

The cold vulcanization of rubber. E. KINDSCHER. *Chem. Ztg.* **45,** 189–91(1921). —A general but fairly comprehensive article dealing historically with the theory and practice of cold vulcanization, including its principal applications. ALAN LEIGHTON

New work upon vulcanizing accelerators. ALBERT BENCKE. *Gummi-Ztg.* **35,** 898(1921).—A summary of the later investigations upon accelerators, dealing principally with the work of Scott and Bedford (cf. *C. A.* **15,** 961). The conclusions are: (1) All org. accelerators become effective through the formation of polysulfides. (2) All org. bases and compds. which form bases during the vulcanization process produce polysulfides with the aid of H_2S. These represent the polysulfide class of accelerators. (3) Thiurate, dithiocarbamate, thiuram and mercaptan form polysulfides directly or with the intermediate formation of disulfide and constitute the group of the carbosulfhydride polysulfide accelerators. (4) The function of the secondary accelerators, such as lead white and zinc oxide, depends upon the decompn. of the polysulfides into colloidal S and amine. (5) Inorg. substances such as NaOH, $Ca(OH)_2$ and $Mg(OH)_2$ react as primary accelerators through the formation of inorg. polysulfides. ALAN LEIGHTON

Elongation at constant load as measure of the state of cure. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* **3,** 246–8(1921).—A comparison of the stress-strain curves for vulcanizates produced by curing a mixed sample of smoked sheets with S at 138° for 6 different periods of time over the range 105 to 165 mins. (corresponding range of S coeffs.: 3.48 to 5.86) shows the following: (*a*) A linear relation between on the one hand either the time of cure or the S coeff. and on the other hand the elongation either at 60, 104 or 130 kg./cm². The elongation at a fixed, intermediate load gives a measure of the rate of cure; and this holds even if the load chosen (say 60 kg./cm².) lies at the bend of the curve. (*b*) A fall in the slope occurs with increase in the time of cure—from 36.8 to 30.8 over the range mentioned (cf. *C. A.* **14,** 3822). In the region of max. tensile strength a variation in the state of cure corresponding to about 0.5 in the S coeff. changes the slope by about 2 units. G. S. WHITBY

Judging rubber from the exterior. O. DE VRIES. *Rubber Age* (Highland, N. Y.) **9**, 127–8(1921); *Rubber Age* (London) **2**, 105–6(1921).—Points out that to evaluate plantation rubber by its appearance is unsound, and gives examples of the anomalies and absurdities associated with valuation on such a basis. G. S. W.

Raw or reclaimed rubber. F. AHRENS. *Gummi-Ztg.* **35**, 928–9(1921).—A review from the economic standpoint of the methods of rubber reclamation together with a discussion of the material available for regeneration and the usefulness of the product. Under present conditions reclaimed rubber cannot profitably be used except where it is actually superior to raw rubber, as in goods to be subjected to high temperatures. The prediction is made that a change in production costs will again soon make the use of first class reclaimed rubber economically possible. ALAN LEIGHTON

Moldy sheet and the effect of mold on quality. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* **3**, 97–8(1921).—The moldy portions of a sample of smoked sheet affected with a light mold were found to cure less quickly than the clean portions of the same sheet, the curing times being 132 and 117 min., resp. G. S. W.

Mold on sheet rubber. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* **3**, 243–5 (1921).—In tests on 2 sets of samples it is found that the vulcanizing properties of smoked sheet are unaffected by soaking for 20–40 mins. in (*a*) a 2–4% soln. of a preservative believed to owe its efficacy to HCHO, (*b*) water. G. S. W.

Rubber coagulated with acid extracted from coconut shell and husk. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* **3**, 245(1921).—A sample of smoked sheet prepd. by the use of pyroligneous acid prepd. from coconut shell and husk gave satisfactory vulcanization results. (Cf. *C. A.* **11**, 2417.) G. S. W.

The rubber industry as a user of dyes and coal-tar products. FREDERIC DANNERTH. *Am. Dyestuff Rep.* **9**, No. 1, Sec. 2, 14–7(1921).—Up to the present the rubber industry has looked to the coal-tar industry principally for organic accelerators such as aniline and thiocarbanilide but there is apparently a wide field for many coal-tar dyes as substitutes for the mineral pigments such as Fe_2O_3, Sb_2O_3, chrome yellow, ultramarine, ocher, umber and sienna. S. D. KIRKPATRICK

Fabrics impermeable to hydrogen (U. S. pat. 1,378,804) **25**.

Vulcanizing rubber. S. J. PEACHEY. Brit. 162,429, Feb. 12, 1920. Addition to 129,826 (*C. A.* **13**, 3040). The cold vulcanization process described in the principal patent is modified by the application of one or both of the gases used at a pressure greater than that of the atm.

Preserving rubber. H. P. STEVENS. Brit. 162,528, Apr. 16, 1920. Vulcanized rubber is preserved by being kept in an atm. which is artificially moistened, preferably up to the satn. point.

Spongy rubber. C. L. MARSHALL. Brit. 162,176, Apr. 15. 1920. In the manuf. of porous expanded rubber by vulcanization in an inert gas under high pressure, a wax or resinous substance, such as ceresin, is added to the ingredients to minimize the diffusion of gas from the spongy mass. The wax or resin may be omitted from the outer layer, which then gradually loses its gas and forms a resilient skin, which prevents excessive expansion of the interior mass. A suitable construction is specified.

Lubricating tire casings. W. F. RAY. U. S. 1,377,729, May 10. Gasolene is used as a carrier for coating and impregnating the surface of rubber tires with pulverized mica.